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NOTICES.

The Institution as a body is not responsible for the statements of opinion expressed in any of its publications.

Copyright.—Publication of abstracts of Papers and articles appearing in the Journal is permitted, provided that acknowledgment is made to the Institution of Petroleum Technologists.

Papers and Articles.—The Council invites Papers and Articles both for reading at Ordinary Meetings of the Institution and for publication in the Journal. All Papers, whether for reading or publication, will be submitted to a referee appointed by the Publication Committee.

The Institution has published a brochure "Instructions for the Guidance of Authors" containing details of recommended practice in the preparation of Papers for publication. Copies of this brochure will be supplied on request.

Pre-Prints.—Advance proofs of Papers to be read at Ordinary Meetings are generally available about a week before the Meeting. Members wishing to be supplied with these pre-prints are requested to notify the Secretary.

Abstracts.—Members and Journal Subscribers desirous of receiving the Abstracts printed on one side of the paper only, can be supplied with these at a charge of 10s. per annum per copy, payable in advance.

Issue of Journal.—Members whose subscription is not in arrear receive the Journal free of cost. A member whose subscription is not paid by March 31st of the year for which it is due is considered to be in arrear.

Changes of Address.—Members are requested to notify any change of address to the Secretary.

Benevolent Fund.—The Benevolent Fund is intended to aid necessitous persons who are or have been members of the Institution, and their dependent relatives.

The Fund is raised by voluntary annual subscriptions, donations, and bequests, and all contributions should be sent to the Secretary of the Institution at Aldine House, Bedford Street, London, W.C. 2. The Fund is administered by the Council through the Benevolent Fund Committee, and all applications in connection therewith must be made on a special form which can be obtained from the Secretary of the Institution.

Appointments Register.—A register of members requiring appointments is kept at the offices of the Institution, and every effort is made to assist members of the Institution in search of employment.

Members who desire their names and qualifications to be included in this register are requested to apply to the Secretary for the Form of Application for Registration, if they have not already done so. Members residing in the London area are asked, if possible, to return this Form in person and make themselves known, together with their requirements, to the Secretary. It is also requested that members should notify the Secretary immediately they have obtained an appointment.

In submitting names of candidates to prospective employers it is understood that the Institution accepts no responsibility and gives no guarantee.

Library.—The Institution's Library may be consulted between the hours of 10 a.m. and 5.30 p.m. daily. (Saturdays, 10 a.m. to 12 noon.)

GENERAL MEETINGS.

General Meetings of the Institution will be held on the second Tuesday in each month at 5.30 p.m. at the Royal Society of Arts, John Street, Adelphi, London, W.C. 2.

Tea, coffee and light refreshments will be provided at 5 p.m. prior to each meeting.

Members may introduce visitors.

Mar. 12*th*. **Annual General Meeting and Induction of New President.**

April 9*th*. **"The Boundary Friction of Oxidised Lubricating Oils."**
Dr. E. R. Redgrove, Ph.D., B.Sc., M.Inst.P.T.

May 14*th*. **"Drilling Muds."**
P. Evans, F.G.S., A.M.Inst.P.T., and A. Reid, A.M.Inst.P.T.

INFORMAL DINNERS.

An informal Dinner is held at Gatti's Restaurant, King William Street, Strand, W.C. 2, immediately following each General Meeting of the Institution, to entertain the authors of Papers.

A cordial invitation is extended to all Members of the Institution.

The cost of the Dinner is 5*s*. (exclusive of wines). No separate notification of these Dinners will be issued.

STUDENTS SECTION.

(London Branch.)

Meetings of the Students Section (London Branch), unless otherwise notified, will be held at the Institution offices at 6.15 p.m. on the dates specified below.

Feb. 28*th*. Visit to The Gas Light & Coke Co., Beckton Works.
Annual Dinner.

Mar. 8*th*. **"The Structural Conditions of Oil Accumulation in Europe."** Symposium.

Mar. 22*nd*. **"Health Hazards in the Petroleum Industry."**
J. McConnell Sanders, F.I.C., F.C.S. (Vice-President).

May 7*th*. **"Crooked Holes."**
A. J. Haworth (Student).

May 21*st*. To be announced later.

Tea and light refreshments will be provided at 5.30 p.m. prior to each meeting.

The Committee of the Students Section extends a cordial welcome to all Members of the Institution to attend the meetings of this Section.

NEW MEMBERS.

The following have been elected or transferred, subject to confirmation in accordance with By-Laws, Sect. IV, paras. 14–15, since the last issue of the *Journal*.

Members.

McLUCKIE, Alexander	Glasgow.
PARRISH, John	London.
MOSEY, Harold Yeoman	London.

Transfer to Member.

HAGUE, Ernest Noel	Sunbury-on-Thames.

Associate Members.

BISKE, Victor	Chester.
GOURLAY, Cleland	Glasgow.
SMITH, Alfred Edward Charles	London.

Transfer to Associate Members.

BEKHOR, Salim David	Baghdad.
FORD, George William	West Bromwich.
HANDS, Clifford Henry George	Sunbury-on-Thames.

Students.

GREGORY, Douglas	London.
RIGDEN, Peter Montgomery	Sunbury-on-Thames.

NOMINATIONS FOR MEMBERSHIP.

The following nominations for membership of the Institution of Petroleum Technologists were approved by the Council on 12th February, 1935, and the application forms may be seen at the offices of the Institution.

The names of the Proposer and Seconder are given in parentheses.

As Members.

DINTILHAC, Jean Georges, Administrateur delegue, Yacco S.A.F. 1, Avenue Marechal Maunoury, Paris, 16e, France. (P. Dumanois; H. Weiss.)

ROGERS, Lewis William, Engineer, 36, Richmond Hill Court, Richmond, Surrey. (F. W. Penny; G. Elias.)

As Associate Members.

COLE, Robert Alfred Leslie, Chemist, 16, Albany Road, Manor Park, London, E. 12. (A. W. Cox; W. F. Jelffs.)

SMITH, David Livingstone Ramsay, Asphalt Plant Superintendent, 22, Sherwin Road, Lenton, Nottingham. (J. R. S. Hawker; D. C. Broome.)

WILSON, Frank William, Chemist, "Clematis," Lower Stoke, Rochester, Kent. (T. Cohn; G. R. Nixon.)

As Transfer to Associate Member.

ROBERTS, Lawrence George Melville, Engineer, BM/LEROY, London, W.C. 1. (A. E. Dunstan; J. Kewley.)

As Associate.

BARBER, Geoffrey Eric, Representative, Trinidad Leaseholds, Ltd., 43, Lyndhurst Avenue, Mill Hill, London, N.W. 7. (J. F. F. McQueen; W. B. Heaton.)

BURMA.

The Council is pleased to be able to report that arrangements are in hand to complete the formation of a Branch of the Institution in Burma.

A well-attended meeting of members and others interested in the proposal to form a Burma Branch was held at Yenangyaung on the 24th January, 1935. This meeting was unanimous in its welcome for the project, and proceeded to appoint the following office-bearers and Members of Committee:

Chairman: Mr. G. W. LEPPER, B.Sc. (Lond.), A.R.C.S., F.G.S.

Deputy Chairman: Mr. W. E. V. ABRAHAM, A.R.C.Sc.I., B.Sc., F.G.S., M.A.I.M.E.

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Members of Committee: Messrs. T. J. F. ARMSTRONG.
J. L. BENARD.
G. C. COTTON.
R. C. PARKER.

Correspondence in connection with the Branch should be addressed to the Hon. Secretary, Mr. C. E. Keep, c/o British Burma Petroleum Co., Ltd., Yenangyaung, Upper Burma.

SUMMER MEETING AND ANNUAL DINNER.

A Summer Meeting of the Institution will be held in London on Friday, 28th June, 1935. Further details of this meeting will be announced in a subsequent issue of the *Journal*, but it is proposed to devote two sessions to the discussion of the Annual Reports on the Progress of Naphthology.

The Annual Dinner will be held at the Park Lane Hotel on the evening of Friday, 28th June.

JOINT MEETING WITH INSTITUTION OF AUTOMOBILE ENGINEERS.

A Joint Meeting will be held with the Institution of Automobile Engineers and other Technical Societies on Tuesday, 5th March, 1935. The subject for discussion is "Cold Pressing and Drawing." Two Papers will be presented by Dr. H. Gough, D.Sc., F.R.S., and Dr. C. H. Desch, D.Sc., F.R.S., dealing with the subject from the mechanical and the metallurgical point of view respectively.

The Meeting will be held in the Hall of the Royal Geographical Society, Kensington Gore, S.W. 7, at 7 p.m. The Chair will be taken by Sir Harold H. Carpenter, M.A., D.Sc., F.R.S.

Advance copies of the Paper may be obtained from the Secretary, The Institution of Petroleum Technologists.

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

At the recent inaugural ceremonies of the Iraq–Mediterranean pipeline, Sir JOHN CADMAN, G.C.M.G., was invested by the Emir Abdullah of Transjordan with the title of Pasha, First Class, and by H.M. the King of Iraq with the Order of the Rafidain, First Class. The third-class Order of the Rafidain was also bestowed on Mr. G. W. DUNKLEY, O.B.E., and the fourth-class Order on Mr. E. A. SATCHELL and Mr. W. E. D. COLE.

Mr. J. L. BENARD has left Burma and is now in Holland.
Mr. D. N. MCKINLAY has left Persia and is in Iraq.
Mr. H. R. MITCHELL is home from the Gold Coast Colony.
Mr. J. T. WARDE is home from Mexico.

The Secretary would be glad to learn of the addresses of the following members: J. M. BROWN, A. F. H. GEE, M. JAWAD JAFAR, J. CECIL JONES, E. L. LEITES, P. B. M. LINTON, A. MACLEAN, B. F. N. MACRORIE, W. J. REYNOLDS, W. MCKECKNIE ROBSON, K. A. SPEARING, and J. TOWERS.

STUDENTS MEDAL AND PRIZE.

Papers submitted for the Students Medal and Prize awarded annually by the Council of the Institution must be received not later than **30th September, 1935.** Two copies of each Paper must be forwarded to the Secretary of the Institution.

The Medal and Prize are awarded for a Paper of a scientific or technical character on a subject connected with petroleum technology, provided that a paper of sufficient merit is submitted.

STUDENTS PRIZE PRESENTED BY MR. T. C. J. BURGESS.

Mr. T. C. J. Burgess has made a donation of £30 to the Council of the Institution for the provision of Prizes for the Students' Section to the value of Ten Pounds in each of three years. The Council will make the first award of these Prizes in the Autumn of 1935, provided that a Paper of sufficient merit is submitted.

The Prize is offered for a Paper on some aspect of the petroleum industry. Students may choose their own subject, but for their guidance the Council has approved the following as being indicative of the type of subject for Papers to be submitted for the Prize :

(*a*) Petroleum Rules and Regulations in different countries.
(*b*) The Transport and Distribution of Oil.
(*c*) The Marketing of Oil.
(*d*) Oil Monopolies in different countries.
(*e*) The Influence of Science on the Petroleum Industry.
(*f*) The Influence of Legislation on the Petroleum Industry.

In choosing the Paper for the Award the Council will pay special attention to originality, constructiveness, and value to the petroleum industry.

The Prize is open to all Student Members of the Institution registered as such at any time between 1st January and 30th September, 1935.

Papers must be addressed to the Secretary of the Institution and received not later than **30th September, 1935.** Two copies must be forwarded of every Paper submitted.

CONTENTS OF MARCH JOURNAL.

The following Papers will be included in the March issue of the *Journal*:

"Sulphur Compounds of Technical Interest. The Isomeric Thiophthens." F. CHALLENGER and J. B. HARRISON.
"Cold Test for Fuels." B. H. MOERBEEK and A. C. VAN BEEST.
"Relative Efficiencies of Packed Fractionating Columns." P. DOCKSEY and C. J. MAY.
"Oil-Field Water Analysis. Part V. The Estimation of Potassium." W. R. WIGGINS and C. E. WOOD.
"Some Viscometric Measurements on Clay Suspensions." G. D. HOBSON.

ARTHUR W. EASTLAKE.
Honorary Secretary.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

THE Thirty-eighth General Meeting of the Trinidad Branch of the Institution of Petroleum Technologists was held at Leaseholds Club No. 1, Pointe-a-Pierre, on Wednesday, 28th March, 1934, Mr. G. H. Scott in the Chair.

The following paper was presented :

ABSORPTION.

By A. NEWTON.

Two absorption processes are in general use for recovering gasoline from hydrocarbon gases—charcoal and oil absorption. This paper is not so much intended to be a description of these processes as a brief discussion of certain principles and experiences connected with them.

There is no necessity to enter into the reasons for gasoline recovery. The modern demand for this product renders it imperative that every possible source should be exploited, quite apart from those ethical considerations which demand the fullest possible utilisation of irreplaceable natural products.

The specification of finished gasoline determines the extent to which the individual hydrocarbons of natural gas may be recovered. Methane and ethane are worthless. Fortunately, they are not readily absorbed, and in any case are easy to fractionate out of the gasoline. Propane boiling at — 45° C. is actually harmful, as exceedingly efficient fractionation is required to remove it, and when left in the gasoline it causes excessive evaporation loss. Moreover, for every 1 per cent. less propane in a gasoline about 3–4 per cent. more *n*-butane may be included without increasing the vapour pressure—a very important consideration when excess butane is available. *iso*Butane boiling at — 11° C. is also of very little use. The first valuable hydrocarbon is *n*-butane, but the proportion that may be included is limited by the vapour-pressure specification of the finished absorption gasoline, which, in turn, is governed by the nature of the material with which it is to be blended. All higher hydrocarbons may be recovered—that is, pentanes, hexanes, heptanes, and octanes—the last of which is the highest hydrocarbon that has been detected in natural gas, and that only in traces.

THE CHARCOAL PROCESS.

The first references to the adsorptive powers of charcoal were made by Fontana in 1777 and by Karl Wilhelm Scheele at about the same date, but the successful commercial application of this property is of com-

paratively recent date. The adsorbent is prepared by carbonising the retorts, and then activating either by treating with steam at about 1000° C. or by saturating with zinc chloride or phosphoric acid and steaming at about 500° C. Numerous variations of these basic methods have also been patented. As a point of local interest, charcoal made from coconut shells shows outstanding adsorptive power.

A charcoal plant consists essentially of two or more vessels—the adsorbers—each of which goes through a cycle of operation. This consists in passing the wet gas through the charge of activated charcoal until the " break point " is reached—that is, until gasoline appears in the exit dry gases. A rather interesting method of detecting the break point has been introduced in some benzole recovery plants. The exit gases from each adsorber are piped to the plant laboratory, and connected to a flat-flame burner. As long as the benzole is being completely adsorbed these flames are non-luminous, but when the concentration of benzole vapour reaches 0·004 of a gallon per 1000 cu. ft. of gas a luminous fringe appears. This method is used only as an indication, a continuous charcoal testing apparatus being used to determine the exact break point. After saturating, the gasoline is displaced from the adsorbent by passing steam through the charge, the steam and gasoline vapours being condensed and separated.

When gas is first admitted to a charge of charcoal, general adsorption takes place, and the charcoal becomes saturated with all the constituents of the gas. The progress of adsorption is marked by a wave of high temperature flowing through the adsorber in the direction of gas flow, and when this wave reaches the end of the charge the normal flow of dry gas commences, consisting, at this time, largely of methane. Each light hydrocarbon is now displaced in turn as more heavy material becomes available in the wet gas, and is preferentially adsorbed from it, and each successive displacement is marked by another more or less distinct high-temperature wave through the charge. The degree of separation of gas constituents obtained by this successive displacement is considerably sharper than with oil adsorption, but there is still an appreciable amount of overlap. Assuming that it is desired to retain all the *n*-butane in the gasoline, but nothing lighter, this degree of overlap renders it necessary (unless the gasoline is subsequently to be stabilised) to continue passage of wet gas for some time after butane appears in the dry gas, to ensure practically complete displacement of propane and *iso*butane. The loss of butane experienced in this way is smaller than would be the case from unstable gasoline in storage. By virtue of this sharper separation, charcoal gasoline has a lower vapour pressure than gasoline of the same gravity produced by oil absorption from the same gas.

The charcoal process is not strictly one of absorption, but adsorption. The vapour does not form a homogeneous mixture with the adsorbent. It is held on the surface of the charcoal as a layer of liquid about 1 molecule thick, or in a highly condensed and compressed condition not clearly distinguishable from the liquid phase. This is evident both from the great reduction in the volume occupied by the vapour on adsorption and by the fact that an amount of heat at least as great as the latent heat of condensation of the adsorbed material is liberated during the adsorption of the vapour of a pure hydrocarbon from mixture with an inert gas. In

fact, in the case of benzole and other hydrocarbons the total heat of adsorption is about twice as great as the latent heat, so that condensation must be accompanied by some other exothermal physical process. The difference between the total heat of adsorption and the latent heat, usually referred to as the heat of wetting of the charcoal by the condensed vapour, is roughly equal to the heat of compression at very high pressures; in fact, it can be calculated from the thermal quantities involved that the degree of compression suffered by the vapour when 10 grs. of charcoal adsorb 1 ml. of liquid is about equal to that which would be produced, in the absence of charcoal, by a pressure of 37,000 atmospheres. In the case of butane 315 B.Th.U. are liberated per lb. of butane adsorbed. Assuming that 0·2 lb. of butane is adsorbed per lb. of charcoal, 63 B.Th.U. are liberated, or, taking the specific heat of carbon as 0·24, and neglecting the heat carried away by the dry gas during the initial general adsorption period, a temperature rise of about 140° C. would result. Since the adsorptive capacity of charcoal decreases about 1·2 per cent. per degree C. rise in temperature, it is necessary to cool the adsorber, especially during the initial stages when lighter gases are being adsorbed and a correspondingly greater amount of heat generated. Cooling is effected in two ways. The adsorbers are provided with coils, embedded in the charge, through which cold water can be circulated. When the adsorption is completed the water coils serve as closed steam coils to heat up the charcoal and prevent excessive condensation when direct steam is admitted. The other method of cooling is based on regulation of the moisture content of the charcoal. A definite relation exists between the moisture in carbon, its temperature, and the steam pressure; for example, with steam at atmospheric pressure and carbon at 124° C. the latter contains about 3 per cent. of moisture when in equilibrium. Less than 6 per cent. of water at the beginning of adsorption, when the charcoal is at about 120° C., allows intense local heating to take place which cannot effectively be taken care of by cooling water coils, and which, in the presence of unsaturated gases, promotes the formation of gummy material which impairs the activity of the adsorbent. If, however, 15–20 per cent. of moisture is left in, the temperature of the charge falls rapidly during the first 20 minutes of adsorption, the heat produced being taken up by the water as latent heat of evaporation. The moisture content does not interfere appreciably with the process of adsorption, as water is readily displaced by hydrocarbon gas.

Very little appears to be known about the effect of pressure on the adsorptive power of charcoal, but there is reason to believe that on increasing the pressure the capacity increases slightly at first, and then begins to fall off. When completely saturated a good charcoal can adsorb as much as 35 per cent. of its weight of gasoline, but in practice the average saturation of a charge does not exceed 20 per cent., owing to the greatly reduced rate of adsorption.

The life of the charcoal depends entirely on the type of gas being processed, deterioration being caused by sulphur compounds and highly unsaturated hydrocarbons, and, in the case of benzole recovery, by tar fog. Hydrogen sulphide itself in moderate quantities is not highly objectionable, but in presence of oxygen the charcoal catalyses the oxidation

of this gas to elementary sulphur (as in the Claus process of gas purification), which deposits on the charcoal and slowly impairs its activity. Unsaturated hydrocarbons are converted by oxidation and/or polymerisation into gums which act in a similar manner. These difficulties are not, of course, of appreciable importance so far as natural gas is concerned, but in recovering benzole from coal gas they are responsible for a charcoal consumption of 7 lb. or more per 1000 lb. of benzole produced, as against 1 lb./1000 lb. of natural gasoline or about 3 lb./1000 lb. when appreciable quantities of sulphur are present.

The charcoal process is thus best adapted for natural gases containing up to, say, 1 gallon per 1000 cu. ft., and is especially to be preferred to oil absorption for very dry gases.

Oil Absorption.

The use of oil absorption for the recovery of valuable vapours from gases is by no means a new process. An experiment was carried out at the Bradford Road Works of the Manchester Gas Department in 1881 for recovering benzole from coal gas long before the use of benzole as a motor fuel was thought of.

The process consists essentially in passing the gas, at a suitable pressure, into the base of a tower down which absorption oil—lean oil or, as it is sometimes called, the sponge—is flowing, some system of baffles being provided to bring about efficient gas–liquid contact. A proportion of each constituent of the gas is dissolved, the proportion increasing with increasing molecular weight of the hydrocarbon—that is, with decreasing vapour pressure. The solution—fat oil—is collected in a surge tank, from which, after venting off any methane and ethane that has been absorbed together with some propane, it is pumped through heat exchangers against stripped oil and steam heaters into stills, where the gasoline is removed with the aid of direct steam. Stripped oil is withdrawn from the stills and cooled, and starts the cycle again as lean oil. The great advantages of this process are that it is completely continuous, and that some form of absorption oil is almost invariably available where gas is to be processed. Practically any natural or refinery gas can be handled, although oil absorption is not particularly suitable for very lean gases.

The following is a typical example of the behaviour of a natural gas in passing through an absorption plant. The composition of the wet gas in per cent. by volume was methane 83·26, ethane 8·34, propane 4·70, *iso*-butane 1·06, *n*-butane 1·54, pentanes and heavier 1·10. Expressed in Imperial gallons per 1000 cu. ft. the amounts of liquefiable constituents present were : propane 1·10, *iso*butane 0·291, *n*-butane 0·41, pentanes and heavier 0·39. Counting 50 per cent. of the *n*-butane present as permissible in the gasoline, 0·60 gallon of valuable gasoline were present per 1000 cu. ft. of gas. After absorption the dry gas had : methane 85·61 per cent., ethane 9·14 per cent., propane 4·00 per cent., *iso*butane 0·78 per cent., *n*-butane 0·47 per cent., pentanes and heavier nil. Allowing for an 8 per cent. reduction in the volume of gas due to absorption, the rounded percentages of each constituent of the wet gas absorbed were :

methane and ethane nil, propane 22, *iso*butane 32, *n*-butane 72, pentanes and heavier 100. The gallons of each liquefiable constituent taken out per 1000 cu. ft. of gas were : propane 0·24, *iso*butane 0·09, *n*-butane 0·29, pentanes and heavier 0·39, of which a total of 0·54 gallon per 1000 cu. ft. was valuable gasoline corresponding to a 90 per cent. recovery of that present in the wet gas. The percentage composition of the absorption gasoline by liquid volume was : propane 24, *iso*butane 9, *n*-butane 29, pentanes and heavier 38. This would have a vapour pressure of 78 lb./sq. in., and would require efficient stabilisation, after which, assuming the retention of 50 per cent. of the *n*-butane, its vapour pressure would be 21 lb. As in the case of charcoal, absorption is accompanied by liberation of heat, so that a lean oil entering the absorber at 90° F. may suffer a temperature increase of 30° F. in passing down the tower. Since the efficiency of absorption is decreased by about 2 per cent. for each degree F. rise in temperature, a considerable proportion of the lighter absorbed material is expelled, and eventually in part escapes in the dry gases. In order to avoid this, modern absorbers are provided with internal water-cooling coils placed on some of the lower trays.

Almost anything can be used as absorption oil, from kerosine to crude oil, but to obtain the best results it is necessary to conform to certain rather exacting requirements. It can be shown by the application of Raoult's Law to the process of absorption that the fraction of any gas constituent absorbed in a tower containing perfect trays—that is, trays on which the gas and liquid come into equilibrium with one another—is given by the product of a constant—376—the oil to gas ratio in gallons of oil per 1000 cu. ft. of gas, the absorber pressure in lb./sq. in. absolute, and the density of the oil in lb. per gallon, divided by the product of the vapour pressure of the hydrocarbon at the temperature of absorption in lb./sq. in. absolute and the average molecular weight of the oil. This formula indicates two of the requirements of a good absorption oil—it should have as low a molecular weight and as high a specific gravity as possible, although the high gravity requirement is modified by the fact that a lighter oil breaks up more readily in the absorber and provides a greater surface. In order to ensure complete separation of absorption oil and gasoline in the stills, whilst avoiding excessive loss of lighter fractions of absorption oil, the latter should have as high an initial boiling-point as possible. With mineral oils low molecular weight is not compatible with high gravity and boiling-point, so a compromise is required. A medium absorptive oil has I.B.P. 400° F., F.B.P. 600° F., gravity 0·83–0·84, and molecular weight 180–220. Other requirements are : low tendency to emulsify with water and resistance to sludging. While discussing properties it may be mentioned that viscosity furnishes an excellent check on the condition of the oil in use, as thickening goes hand in hand with loss of absorptive power.

The treatment of natural gas is a comparatively simple matter. The gas does not usually require compression, and unless air lift is being employed in some of the contributing wells it seldom contains appreciable amounts of oxygen. Refinery gas is an entirely different proposition. It may contain as much as 12 gallons of gasoline per 1000 cu. ft. (about 40 per cent. of the total gas volume) up to 50 per cent. of air, considerable

quantities of corrosive hydrogen sulphide, and traces of equally corrosive mercaptans. In the case of cracked gases it is also highly unsaturated, and may contain gum-forming constituents. Trouble starts with compression, for, if the absorber pressure is fairly high—that is, of the order of 100 lb. absolute—the final condition of the gas will almost certainly be above its dew-point, and liquid gasoline may separate even before complete cooling. If the compressors are of the reciprocating type, cylinder lubrication becomes almost impossible, as the lubricant is immediately washed off the walls by condensed gasoline. The difficulty can only be eliminated by choosing an absorption pressure such that the compressed gas is not appreciably above the dew line. To give a concrete case, a refinery gas containing about 8 gallons of gasoline per 1000 cu. ft. was compressed in two stages of 0–30 and 30–135 lb. gauge. The low-pressure stage gave no trouble, but the high-pressure compressor, after running for about 50 hrs., showed all the signs of having been run completely dry. Low-pressure absorption—30 lb. gauge—was finally adopted, and with suitable changes in other absorber conditions proved entirely satisfactory. The high-pressure compressor that formerly gave so much trouble is used for the low-pressure stage, and runs continuously for weeks.

The second major source of trouble is corrosion. Hydrogen sulphide as such is not by any means the chief offender in this respect. In presence of air the heat of compression accelerates the oxidation of hydrogen sulphide, mainly with production of elementary sulphur, but also of small quantities of sulphur dioxide and sulphuric acid. The sulphur deposits in the gas coolers, and in presence of moisture becomes soaked with dilute sulphurous and sulphuric acids, which corrode the tubes and shell of the cooler. A deposit resulting from this action was found to contain 24 per cent. of iron and 52 per cent. of sulphur, part of the latter being present in the form of well-defined, pale yellow crystals.

Hydrogen sulphide itself is also responsible for corrosion. It forms a scale of ferrous sulphide on pipes, absorbers, and stills, which may be a thin hard layer, which is to some extent protective against further action. On the other hand, after being oxidised to free sulphur it contributes to the formation of a deposit by the absorber oil, which tends to build up on bubble caps and overflow pipes, and may gradually reduce the capacity of the plant, causing considerable entrainment. This sediment is a black finely-divided material, which is carried round in suspension in the absorption oil until it comes to a place where it can adhere or where the oil is comparatively quiescent, as in the fat oil vent tank or the bases of the absorbers and stills where it deposits. It appears to be a good emulsifying agent, and where water is present a frothy oil–water emulsion stabilised by the sediment is formed. The dry material, which is mainly carbonaceous, may contain up to 15 per cent. of sulphur, and usually has a very low metal content of the order of 2–3 per cent., so that corrosion is a relatively small factor in its formation. Reports of similar sludge formation in absorption oil have frequently attributed this occurrence to oxidation, but it has been found, at least in the case under consideration, that the oil shows little or no tendency to oxidise under plant conditions, but that sludge corresponding closely in composition and appearance to that found in the plant can be produced readily and repeatedly from the same oil by

heating it with successive quantities of elementary sulphur. A paraffinic oil behaves best as regards resistance to sulphurisation, and has the least tendency to form asphaltic sludge, but no type of hydrocarbon is wholly immune from the action of sulphur.

In this connection several advantages, notably higher adsorptive capacity and resistance to sludging, have been claimed by Bregeat for other adsorption media, such as a mixture of cresols of sp. gr. 1·04 or tetrahydronaphthalene, but these are relatively expensive, and are not likely to displace mineral oil, especially in refineries.

To prevent sludge formation it is thus necessary to remove either the oxygen or the hydrogen sulphide from the gases. In order to ensure practically complete exclusion of air from a gathering system, it would be necessary to regulate the suction on each separate tank or other source of gas in the system according to the vapour pressure of the contents—by no means an easy matter. At first sight, removal of hydrogen sulphide appears to be the obvious solution, but this is complicated by the fact that refinery gases may contain more carbon dioxide than hydrogen sulphide. The presence of carbon dioxide is not objectionable in the plant, but it is absorbed by any alkaline washing solution, together with the hydrogen sulphide, and if the solution is used to exhaustion tends, on account of its more acidic nature, to displace the dissolved hydrogen sulphide back into the gas stream. At the best the consumption of alkali is unnecessarily increased in the proportion of the carbon dioxide content of the gas. For this reason the most economical practical washing agent is water, which dissolves about four times as much hydrogen sulphide as carbon dioxide, but which, on account of its relatively low solvent power for either gas and the fact that the small partial pressures of these gases are significant in a process of purely physical solution, must be used at as high a pressure as possible.

In conclusion, I have to acknowledge my indebtedness to the work and ideas of several members of the staff of Trinidad Leaseholds, Ltd., notably Mr. James and Mr. Finnis, and to Messrs. Trinidad Leaseholds, through Mr. Johnston, for permission to include the account of experiences on the Company's absorption plant.

DISCUSSION.

Mr. I. McCullum said he had a few criticisms to make, and would like particularly to comment on the figures which were given as a typical example of absorption plant conditions. The Author stated that no methane or ethane was absorbed by the oil from the wet gas, making use of the formula given in the paper. The speaker found that theoretically about 2 per cent. of ethane was taken out, and 2 per cent. on 85 per cent. represented a very considerable quantity. It was their experience that for every gallon of gasoline produced 40 cu. ft. of non-condensible gas was evolved and was re-cycled to the absorber. Unfortunately, they had no facilities for the fractional analysis of gas, but in view of the fact that this gas had a density of 1·05, it was obvious that ethane must be present, and no doubt methane as well. He could not imagine any set of plant

conditions under which methane and ethane would not be absorbed in measurable quantity. It was said elsewhere, rather contradictorily, that any methane or ethane absorbed was vented off from the fat–oil tank. Had the Author any information about the quantity of gas so discharged?

A hydrocarbon analysis of the resultant gasoline was then given which showed 62 per cent. of the product to be material gaseous at normal temperatures and pressures. He did not think it right to give such an extremely volatile gasoline as typical of oil-absorption plant output. This seemed to be a rather particular case in which absorption had been pushed to the limit to obtain maximum butane recovery for the purposes of subsequent stabilisation.

The Author mentioned crude oil as a possible absorption medium. This struck him as a very interesting possibility, particularly in view of the fact that it was not always necessary to isolate natural gasoline as such. Crude oil would have a high vapour pressure relative to that of the orthodox absorption oil, and it seemed to him that in order to get anything like efficient recovery fairly high absorber pressures would be required. He would like the Author's opinion regarding the latter point.

The Author mentioned difficulties encountered in compressing wet gas due to the washing of lubricant from the cylinder walls. Castor oil was not appreciably miscible with gasoline, and had been successfully used in such cases where excessive dilution of the lubricant was liable to take place.

Mr. H. E. N. Pracy disagreed with the assumption that the charcoal process was the most efficient for absorbing benzine from natural gas, and gave as an instance his experience with a charcoal plant which appeared, according to the Burrell Absorption Test, to be working efficiently, and gave a dry gas between 0·1 and 0·15 gallon of benzine per 1000 cu. ft. Part of the dry gas which was piped to the refinery was passed through a pressure absorption plant, in which heavy naphtha was used as an absorbing medium and 0·5 gallon per 1000 cu. ft. of benzine was obtained. He suggested that this proved that, in the first case, the Burrell test was not a satisfactory one, at any rate in the tropics, and that, secondly, it was possible by pressure absorption in oil to strip the natural gas much more efficiently.

With regard to the effect of pressure on charcoal absorption, he stated that although he had no information regarding the effect of pressure on the capacity of charcoal, he had found that increased pressure improved the efficiency of the charcoal plant, presumably owing to the reduction of velocity through the plant.

Mr. A. H. Richard said that the Author stated that "fortunately methane and ethane are not readily absorbed." The speaker thought this might read "not as readily absorbed as other hydrocarbons."

The "break-point" was, as the Author said, only really applicable to a benzole plant when dealing, more or less, with one constituent. It would not be applicable to a plant for extracting casing head gasoline. In the first place, there was not the time to wait for a test of that description, and in the second place, as the Author had said, there was a con-

siderable amount of overlap. In a plant for the extraction of gasoline from casing-head gas the normal way was to determine the most economical cycle which would give maximum recovery of marketable gasoline, and then a time schedule could be worked to with very little variation.

He took it that the remarks about moisture in charcoal were essentially applicable to benzole plants; personally he could not see that they referred to gasoline plants.

He understood that the statement about the relation between moisture in the carbon, its temperature, and the steam pressure referred to the end of the distillation, and then the Author went on to say that not less than 15–20 per cent. moisture was required to prevent local overheating. The speaker had the opportunity of visiting the Beckton Plant of the Gas Light & Coke Co., at that time the largest charcoal plant for the recovery of benzole. They had coils for steam and cooling water. Their greatest trouble was unsaturated gases, and formation of gummy material was a function not only of temperature, but also of time, and they therefore reduced the time of regeneration to the smallest possible amount. The schedule they were running on was 3½ hrs. adsorption, 35 mins. steaming, 10 mins. drying. Thus, although they wanted to cut down the time of regeneration, they devoted 10 mins. of that valuable time to drying. He gathered that the Author had some more recent information on the subject, which he would be glad to receive.

In a plant for extraction of casing-head gasoline it was absolutely essential to have the charcoal as dry as possible. He had to admit that the formation of gummy material scarcely came in there.

Mr. Richard then gave some figures which showed the importance of drying in their casing-head gasoline plant. They heated their drying gas in a tubular steam heater. They discovered at one time that the heater was leaking, 5000 gallons of gasoline per day being obtained with the drying gas wetted by steam. They then shut down the heater for repairs and continued running the plant without drying, and the production fell to 4100 gallons. When the gas heater was repaired and put back into service, the production jumped to 6200 gallons, which showed that it was extremely important to have the charcoal as dry as possible. The corresponding gasoline gravities were 0·683, 0·694, and 0·674, which indicated that when the charcoal was less dry its adsorptive capacity was less and the lighter fractions were being driven out. The corresponding figures for the saturation of the charcoal with gasoline were 5·4, 3·8, and 6·0 per cent. by weight. They later improved their drying and cooling systems and obtained 7000 gallons per day. Even that was not sufficiently satisfactory, as the cooling system had been doubled in capacity but not in efficiency, because they were using at the time a water spray tower to re-cool the cooling gas, which in turn wetted the charcoal. They were then getting a percentage of saturation of 6·75 in the charcoal. The spray cooling tower was replaced by tubular coolers, and the capacity of the plant immediately increased by 50 per cent.—in other words, they were able to lengthen the schedule by 50 per cent. to obtain the same production. The percentage saturation jumped to 10 per cent.

Theoretically, moisture would keep the charcoal cool and the heat of absorption would remove the moisture, but, as far as he could see, the

time factor entered, and the rate at which the moisture was driven out was not as great as the velocity of adsorption. One could not possibly use that process without very large absorbers. It was much more economical to spend a little time in drying than to increase adsorber capacity, say, four times, and wait for the heat of adsorption to do it.

The Author said that "the average saturation of a charge does not exceed 20 per cent." He would like to know the authority for that, as he had not been able to find anything approaching it. Their own experience in tests was that something around 13–14 per cent. was the maximum saturation for maximum recovery. The Carbo Union said that, due to various causes, not more than 16 per cent. of efficient saturation could be obtained. Oberfell and Alden indicated that the limit was 12 per cent. without affecting results.

The Author stated that "the life of the charcoal depends entirely on the type of gas being processed." That was not quite correct; there were other factors entering into it, the major of which was the reactivation of the charcoal. That was a point, as far as he could see, the Author had not touched on at all, and it was quite an important one. In their plant they soon found that the charcoal was progressively lessened in activity, and that if they were going to keep down costs it must be reactivated. They designed a plant for the purpose, and by that means they increased the life of the charcoal enormously. The Author mentioned 1 lb. of charcoal per 1000 lb. of gasoline. By reactivation they had got their consumption down to 0·4 lb. per 1000, at least 75 per cent. of which was due to the mechanical disintegration in handling.

It had been borne out by their experience that charcoal did act as a catalyst in depositing free sulphur in the presence of oxygen and that high temperature aided the reaction. Advantage had been taken of that to pass the incoming rich gas from the compressors to the purifiers at a temperature of 60–70° C. before going to the rich gas coolers.

The Author stated that a charcoal plant was thus best adapted for natural gases containing up to 1 gallon per 1000 cu. ft. He did not quite see the point of the word "thus." He did not see any reason at all—and he was supported by the opinion of the makers of the plant—why a charcoal plant should not be used for gases containing 8–10 gallons per 1000 cu. ft., except that the size of the plant might become somewhat unwieldy. He rather thought it was the attitude of mind engendered in those who were in favour of the oil absorption plant. The oil absorption plant is better suited to gases richer than 1 gallon, than to those leaner than 1 gallon, and, therefore, they say the charcoal plant is not good for gases richer than 1 gallon.

He would like to inquire the reason for going to 135 lb. pressure with such a rich gas as 8 gallons per 1000 cu. ft.

The Author's phrase "the compressed gas was not appreciably above the dew line" should be qualified by the words "at the temperature of compression."

Washing of the lubricant would be the same with rotary compressors. The Turbo blower type would possibly be free from trouble. As Mr. McCullum said, it was a question of proper lubrication. They found castor oil was excellent up to 70° C., and they knew it was not good at 125° C.

He would like Mr. Newton to tell them the temperature of the gas when leaving the second stage at 135 lb. He was not quite sure what the vapours were, and he did not know the temperatures. It rather appeared to him that the trouble was due not so much to condensation in the second stage, but in the intercooler. It seemed to him more probable that condensate from the intercooler might have been allowed to go into the cylinder. He did not think that at 135° C. that amount of liquid could be condensed.

The Author mentioned 50 per cent. of air in refinery gases. He would like to inquire why that large percentage of air was allowed to go in. On the face of it the effective compressor and plant capacity was reduced 50 per cent. Connected with that, it was stated that to regulate the suction on each separate tank or other source of gas in the system according to the vapour pressure of the contents was by no means an easy matter. He did not quite see where the difficulty came in. They had no trouble of that description at all. They grouped their tanks into batteries, with the vapour line manifolded. One regulator—a low-pressure sensitive relief valve—relieved vapours into the suction line and prevented a vacuum being pulled on the tanks. The vapour line manifold provided against air being sucked in when emptying one tank of the group.

Sometimes they might have 1 per cent. of air in the gas, but generally there was none. Of course, vapours from crude oils were at more or less atmospheric pressure, but even with distillates of higher vapour pressures it would be fairly easy to set the relief valve to something just above the vapour pressure of the liquid.

Mr. Richard, in reply to Mr. Banks, said that, when necessary, in the large storage tanks, rich or stripped gas was used for re-pressuring.

Mr. W. I. Malcolm Brown queried the Author in regard to optimum oil-gas ratios in oil absorption plants, and also asked if he could give them any figures on the actual heat of absorption.

Mr. B. G. Banks stated that the Author had rather over-stressed the need for preventing sludge formation in absorption plants, and that in practice it was usual to pass, say, 25 per cent. of the amount circulated daily through a small steam-heated vacuum still, and in that way ensure the plant being kept comparatively clean.

In connection with Mr. Richard's remarks about the trouble experienced by air getting into the plant, this was due to the fact that no re-pressuring of the tanks was practised in the plant referred to by the Author, and that the tanks, when they cooled down at night, drew in air from outside, and this was passed out into the gathering system as they warmed up inside.

Mr. R. Godfrey said he thought the prevention of corrosion in an absorption plant was very important, and could be effected only if one had a complete knowledge of the construction of each unit comprising the plant.

Apparently the Author had only considered a plant equipped with stainless steel tubes, which were necessary if large quantities of hydrogen sulphide were to be handled, as in refinery gas, etc. In natural gas

absorption plants equipped with copper alloy tubes, the formation of copper sulphide was very rapid, if one did not exercise great care in keeping the sulphur content of the absorption oil to a minimum.

In a refinery this presented no difficulty, but if a small fire still was used to produce the absorption oil, the oil should be run through a NaOH scrubber to eliminate the possibility of formation of elementary sulphur.

The sludge which was formed, as well as settling oil in the fat oil-vent tank and absorber, deposited on the coils of the lean oil coolers, considerably reducing their efficiency.

Analysis of water from the dehydrator and gasoline accumulation invariably showed small quantities of iron, indicators that corrosion was taking place in the still, coolers, and condensers.

This was accounted for by the fact that some of the CO_2 in the gas found its way into the still and was dissolved in the condensed steam. Here again, for a chemical action to take place, free oxygen must be present. Hence, by the exclusion of air, another source of corrosion was eliminated. If, however, any bi-metal fittings were used in the distillation system, such as brass-seated unions, etc., electrolytic action took place and leaks soon developed. This could be overcome only by using all iron fittings.

It was impossible to stop some of the lighter ends of the absorption oil coming over with the gasoline, and with continual make up, the heavy ends collect in the system. These could be got rid of by running a continuous redistillation system in conjunction with the plant. This method was fully explained by Kay and Sellers (*Petr. Eng.*, Mar. 1933, **3** (6), 64); briefly, it consisted of continually bleeding off a small quantity of oil from the base of the still, distilling it, and returning the condensate to the system. The heavy ends collected in the still, which was dumped periodically. This method totally eliminated shut-down time for changing oil, kept the system clean, and resulted in a greater overall efficiency.

Mr. C. E. Capito stated that the Author had said that most of the propane and butane had to be eliminated from the gasoline. He had recently received a very interesting letter from California, in which it was stated that large quantities of propane and butane had been injected with the natural gas into the oil strata, and these experiments had been so successful that cores taken from a sand which was originally heavily saturated with crude oil were found to be so clean and barren of oil as not to discolour ether. He wondered to what extent propane and butane not wanted in gasoline in Trinidad could be used for cleaning out oil-sands, and if the Author could give him any idea of the quantity of these gases that would be available.

Mr. A. Newton, replying, said that in regard to Mr. McCullum's point about the vapour pressure of gasoline recovered from natural gas, it was a known fact that such a gasoline frequently had a pressure of 15–20 lb., and was used for blending, not for direct use. When referring to crude oil as an absorption medium, he did so particularly in regard to its use as a stripping agent for gas, for which there was no other means of recovering gasoline, in which case the crude would not be recovered and used again.

As regards the use of castor oil as a lubricant, he was aware of that, as he had quoted it in the paper, but it was just as useless as mineral oil lubrication. He also tried a strong solution of caustic soda. Nevertheless, the cylinders were always dry after a short run.

He was very interested in Mr. Pracy's account of the use of oil absorption plant after charcoal. He understood there had been suggestions that the charcoal plant should rather be capable of being used for gasoline recovery from the exit gases from oil absorption plants, and he believed that a charcoal plant was in use for that purpose. As he mentioned in the paper, very little information was available as to the effect of pressure on charcoal absorption. What he referred to particularly was not so much rate of absorption as the ability of the charcoal to hold more gasoline under pressure. The remarks in the paper must be considered to hold for that point.

The plant referred to by Mr. Richard was the Beckton Plant of the Gas Light & Coke Co. That plant recovered 3,000,000 gallons of benzole a year, and according to a paper by the people in charge of that plant published about six weeks ago, it was their practice to leave 20 per cent. of water in the charcoal at the end of steaming, that was at the beginning of the absorption period. He had no other information as to how this would affect gasoline recovery, and must refer to Mr. Richard's experience in that line. His information on the saturation of the charcoal was derived chiefly from the paper by Edeleanu (*J.I.P.T.*, 1928, **14**, 296). His remarks on the consumption of charcoal did not take into account reactivation, so those figures referred to the first use of the charcoal or from one reactivation to the next.

Mr. Richard stated that charcoal absorption was quite suitable for very rich gases. The Author did not question the efficiency of charcoal absorption for dealing with gases with any gasoline content. He had no figures in support of the statement, but he believed that capital expenditure and operating costs of the charcoal plant for gas of very high gasoline content would be greater than for an oil absorption plant.

The reason for the use of absorption at 135 lb. pressure was that by far the greater volume of the gas to be processed was available at this pressure, and it was hoped to process other refinery gases and tank gases through the same absorber.

Regarding the question of deposition, gasoline was actually deposited in the cylinder; the place in which the condition of the gasoline must be above the dew line was in the cylinder. In the case quoted, the temperature of the gases from the high-pressure stage was 130° C. before going into the cooler, so that even at that temperature some gasoline was deposited. This gasoline did not come from the inter-cooler, as drain traps were provided in the coolers, and those traps were always bled before the level was high enough to permit carry-over from inter-cooler to high-pressure cylinder.

The question of excluding air from the refinery gathering system was rather a different matter than when dealing with a field tankage system. Fifteen to twenty tanks were dealt with by the gathering system, and those tanks might contain anything from crude oil to very volatile gasoline at high temperature and a vapour pressure of about 15 lb., whereas crude

oil vapour pressure might be as low as 3–4 lb. Relief valves had not been found very satisfactory, and considering the wide variety of products handled and the variation of conditions during the night and day, the only certain method of excluding air appeared to be to regulate each tank individually.

Dealing with Mr. Malcolm Brown's query as to the amount of heat liberated by absorption, the Author said he had no figures on this, but taking the specific heat of absorption oil as about 0·5, a temperature rise of about 30° F. corresponded to liberation of 120,000 B.Th.U. from each 1000 gallons of absorption oil circulated.

He had no information on the use of propane and butane for re-pressuring, but he would mention that those gases were by no means waste products, and there was every probability that they might become as useful as absorption gasoline from which they were recovered. They had been used to a great extent for chemical materials, and also for domestic heating and various other uses.

On the motion of the Chairman, a vote of thanks was accorded to the Author, and to their hosts, the President and Members of the Leaseholds Club, for the use of the Building.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

THE Fortieth General Meeting of the Trinidad Branch of the Institution of Petroleum Technologists was held at Apex Club, Fyzabad, on Wednesday, 30th May, 1934. The Chair was taken by Mr. A. Frank Dabell.

The following paper was presented :

SOME NOTES ON BARYTES RECOVERY FROM MUDS.

By G. H. SCOTT, B.Sc. (Assoc. Member).

INTRODUCTION.

Barytes is now being used in increasing quantities as a weighting material for drilling fluids, and the cost per foot of this mineral is a serious item in the drilling expenditure. It is therefore advisable to study the feasibility of recovering this barytes in a fit state for further service.

The relative economic importance of such recovery varies considerably with the operating conditions. In fields, where much of the drilling can be carried out without recourse to loading of the muds, it is possible to use gas cut or highly viscous muds of heavy weight, which would be entirely unsuitable for further service in high-pressure wells, merely by watering them back to a suitable consistency.

In cases where such muds can be re-used in the diluted condition, it becomes necessary to calculate the relative economic efficiency of barytes separation compared with dilution.

To cite an example. It is supposed that a barytes recovery plant has been designed which will recover 85 per cent. of the barytes with a resultant specific gravity of 4·0. One hundred barrels of poor mud weighing 100 lb./cu. ft. are on hand, and it is required to know whether it would be more economical to recover the barytes and make up mud of 85 lb./cu. ft. with it, or to dilute the original mud to that weight. The weight of the original clay mud is supposed to be 70 lb./cu. ft. in all cases.

1. Every cubic foot of 100 lb./cu. ft. mud contains 40·9 lb. of barytes. Of this 85 per cent. or 34·8 lb./cu. ft. can be recovered. Therefore from 100 brl. 34·8 × 560 or 19,500 lb. can be recovered.
2. Commencing with 70 lb./cu. ft. clay mud and loading this to 85 lb./cu. ft. with the barytes recovered, which has a specific gravity of 4 or a weight of 250 lb./cu. ft., we have :

$$70(1 - x) + 250x = 85.$$

$$\text{or } x = 0{\cdot}0836 \text{ cu. ft.}$$

$$1 - x = 0{\cdot}9164 \text{ cu. ft.}$$

Therefore in every cu. ft. of resultant mud there are 20·9 lb. of barytes.

Thus 19,500 lb. will load $\frac{19{,}500}{20{\cdot}9 \times 5{\cdot}6}$ brl. = 166·4 brl.

To dilute 100 lb./cu. ft. mud to 85 lb./cu. ft.:

$$62{\cdot}5x + 100(1 - x) = 85.$$
$$x = 0{\cdot}41 \text{ cu. ft.}$$

Thus every cubic foot of diluted mud will contain 0·41 cu. ft. of added water and 0·59 cu. ft. of the original mud.

Thus the volume of the original mud will be increased from 100 brl. to 169 brl.

Thus, in this instance, taking into consideration the cost of the barytes recovery, it would appear more economical to carry out simple dilution. This, however, presupposes that the increase in volume is required, which is not by any means always the case. In fact, in many fields the bestowal of excess mud is becoming quite a problem. Furthermore, it must not be imagined that the resultant muds are of analogous value, as the one that has been diluted will carry an appreciable sand content which will have been removed in the other.

Even admitting that in some cases dilution is preferable to a barytes recovery scheme, any mud finally reaches a stage, owing to high sand content or other factors, where it can no longer be utilised in any form, and waste mud dams, old slush pits, etc., yield a fruitful supply of mud for treatment.

In many cases, in order to avoid waste of barytes, the use of a mud is persisted with when it has reached a condition which is definitely retarding drilling progress. If one could be assured of recovering the barytes from such a mud, there would be no hesitation in discarding it and using fresh, even if this involved a loss of 15 per cent. by weight of the barytes.

General Schemes of Mud Reconditioning.

The general schemes for mud reconditioning can be divided into two main groups:

1. Dilution, separation of the sand and cuttings, and thickening of the clay barytes suspension.
2. Dilution, separation of the sand, and separation of the barytes.

The first group is most suited to localities where clay for the mud has to be obtained from outside sources and where water consumption is an item of major importance. Owing to the extremely slow settling rates of colloidal clay suspensions, the thickener must be of very large area, and the cost of such equipment would be prohibitive for a small operator. It is true that the settling rate of these clay slimes can be accelerated by coagulation by electrolytes such as alum, but the stability of the resultant thickened mud is liable to be deleteriously affected. It further necessitates that all drilling wells are connected to a central mud farm by a system of duplicate mud lines.

This system is therefore best adapted to localities where large-scale drilling operations are in progress.

In Trinidad it may be stated *a priori* that there is no lack of suitable clays for mud-mixing purposes. In fact, in the majority of wells too much mud is made from the formation traversed. The conservation of the clay portion of a loaded mud is therefore not of very great importance, and in almost all cases it proves to be more economical to waste it rather than to provide equipment for de-watering and thickening. The water consumption is, however, of importance, but once the barytes has been removed, clarification can be accelerated by electrolyte addition, and the coagulum wasted.

Methods of Separation.

All methods of separation depend on the differential gravities of the various constituents of a mud. Those in any way suited to mud treatment may be divided into three main groups:

(*a*) Pneumatic Separation, where a carefully controlled air blast is utilised to separate small grains from powders.
(*b*) Centrifugal Separation.
(*c*) Hydraulic Separation, where the differential settling rate in water is utilised to separate the various constituents.

(a) *Pneumatic Separation* is not ideally suited to muds. It entails the evaporation of the water and pulverisation of the remaining solid content, which is uneconomical. Moreover, the proportional velocities of settling of grains of equal diameter for any two minerals are much less in air than in water.

This is illustrated by the following figures, taken from Richards ("Ore Dressing," Vol. II, p. 826).

	Proportional Velocities of Settling.	
	Quartz.	Galena.
Air	1	2·88
Water	1	4·06

This method of separation should be suited to treatment of the original barytes after grinding to ensure the absence of over-size grains.

(b) *Centrifugal Separation.*—In this method of separation the differential velocities set up in grains of different size and different gravities by the action of centrifugal force are utilised to separate them. There are several centrifugal machines on the market designed for the de-sanding of muds, and recently claims have been made that economical barytes separation is achievable.

Richards ("Ore Dressing," Vol. II, para. 112) shows that the ratios of the velocities of mineral particles under the action of centrifugal force do not vary greatly from those under free settling conditions in water, differing only in the rapidity of the action. Thus it is unlikely that the sorting will yield a cleaner final product, be it sand or barytes.

The Author is of the opinion that if this principle is used it is best adapted to barytes clay separations after removal of the sand. The comparatively

high speeds (approximately 600 r.p.m.) at which these machines run renders the bowls liable to excessive wear if used for de-sanding purposes, and great care will have to be exercised to guard against sand reaching the bearings.

Centrifugal machines have been most widely utilised in the separation of liquids, and have not been widely adopted for ore-dressing purposes for the separation of solids from liquids. It is much more simple to allow for the continuous discharge of a heavy liquid thrown to the circumference of the centrifuge bowl, than for heavy solid particles which will tend to pack into a hard cake.

The following is a summary of the advantages and disadvantages of this method as compared with hydraulic settling:

Advantages:

1. It is more rapid in its action than simple hydraulic settling.
2. The extent of dilution for separation can probably be reduced.
3. The machine can be made more compact and portable.

Disadvantages:

1. High initial cost.
2. Higher running costs which are not liable to be counterbalanced by improved separation.
3. The need for very careful control of the speed of rotation.
4. Higher maintenance costs.
5. The danger of clogging of the heavy mineral discharge.

(c) *Hydraulic Separation.*—It is proposed to deal more fully with this method, not so much from the point of view of giving any basic recommendation for the design and lay-out of a recovery plant, but rather from that of the general principles governing classification by settling in water. Many of these principles are quite applicable to both pneumatic and centrifugal separation, and also to the normal sand and cuttings separation from mud in boxes, ditches, and flumes.

Particles of solid matter settling in water do so subject to two distinct and separate laws according to the solid concentration, namely:

(*a*) Free Settling.
(*b*) Hindered Settling.

These terms are largely self-explanatory. Thus, under free settling conditions the grains fall freely and unhampered in either still water or against an upward rising current, whilst in hindered settling the grains are in a crowded mass, but are still free to move among themselves.

It is of vital importance to understand the basic difference of these two conditions of settling. Both are widely utilised in ore-dressing, but the classification and mineral concentration obtained are fundamentally different.

If grains of minerals of different specific gravity settle at an equal rate in water, the ratio of their diameters can be termed the "settling ratio." Under free settling conditions the settling ratios are always less than under hindered settling. That is to say, any classified product will, under

hindered settling conditions, have a higher percentage of fine-grained heavy-gravity material mixed with the coarser-grained gangue material.

The average free settling ratio of quartz and galena is 3·9 : 1.
" " hindered " " " " 6·9 : 1.

In barytes separation from mud a two-stage classification is necessary :

(*a*) The separation of the sand.
(*b*) " " " barytes from the clay.

In the first stage it is desired to have the spigot product with as little barytes as possible, whilst in the second stage the barytes must have a minimum of clay contamination. If settling takes place under hindered settling conditions, it is obvious that the higher settling ratios will result in an increase in the barytes in the first stage and an increase in the clay in the second stage. It is therefore obvious that free settling conditions must be maintained for optimum results.

Thus, the first prerequisite for efficient barytes separation is that the mud shall be diluted to an extent sufficient to ensure that the individual grains are free settling. The dilution required will obviously be dependent on the solid concentration, the viscosity of the suspending medium, and such like factors, and cannot be assumed to be a constant figure. In the Author's various experiments it has been found that over-dilution is preferable to under-dilution. A manufacturer of classifiers and thickeners to whom a sample of mud was submitted recommended a dilution of 12·3 : 1, whilst it has been found that 10 : 1 is a good average figure. The Author neither wishes to infer that these figures are applicable to other fields, nor that they would necessarily be adopted in operating a full-size plant. It might very well prove more economical to increase the loss of barytes in the sand spigot by 5 per cent. to avoid extra water consumption, tank storage, and clarification reservoirs. In such cases one must be guided by the economic factors.

General Principles of Free Settling.

Factors affecting free settling are summarised by Richards ("Ore Dressing," Vol. II, para. 353) as follows :

(*a*) Specific Gravity : Of two particles of varying specific gravity, the one with the heavier gravity will fall the fastest.
(*b*) Size of Particle : Of two particles, the larger will settle the faster in water.
(*c*) Shape of Particle : Of particles which pass through the same screen, the roundish grain will settle the fastest, followed by the long narrow grain, and then the flat platey grain.
(*d*) Density of Liquid : The rate of fall of particles is more rapid in lighter liquids than in heavy.
(*e*) Viscosity of Liquid : In two liquids of different fluidity the rate of settling is more rapid in the more fluid liquid.

Always provided that the dilution is adequate, the density of the liquid and its viscosity may be taken as that of water. It is possible that the

density may vary with different amounts of dissolved matter such as salt, etc., and the viscosity with varying amounts of gel-forming colloids, but it is considered that after dilution the effect of these on settling rates may be neglected.

Similarly, the shape of a barytes particle is roundish, and can be considered as analogous to that of the normal sand grain.

Thus, the two factors which are of greatest importance in barytes recovery are the size and specific gravity of the particles of sand, barytes, and clay.

Sand: The sand content of a mud has a specific gravity of about 2·6, and the size of the grains varies from 0·2 mm. diameter down to grains of microscopic size. In the Apex field the free sand bodies usually show an excess of 90 per cent. on 200-mesh (larger than 0·063 mm.), but the sand portion of silts and silty clays shows an excess of the fine grains.

Barytes: The normal specification for barytes is a specific gravity greater than 4·15 and a residue of not more than 2 per cent. by weight on a 300-mesh screen. This means that the individual grains vary from 0 to 0·0425 mm. in diameter.

Clay: The clay particles are of sub-microscopic size. Even in fine dispersions they exhibit extremely slow settling rates. The specific gravity is approximately that of the sand.

It might be assumed that the ratio of the diameters of sand and barytes grains which are equal settling would be constant for any velocity of settling. This, however, is not the case. Below a certain critical velocity of settling the grains follow the Law of Viscous Resistance, whilst above that velocity the Law of Eddying Resistance applies. Thus, in the case of barytes and quartz grains the free settling ratio is as low as 1·19 for small grains and reaches as high as 2·0 for the larger grains. In practice, in spite of the higher settling ratios, it is generally simpler to classify two minerals in the medium grain sizes, owing to the fact that the differentials of current velocity which cause the grains to rise or fall are much higher than with small grains. With fine grains, although the lower settling ratios will aid in a finer grading of the sand and barytes with respect to size of grain, the range of velocities which will alter a rising condition to a falling condition for any size of grain is of such a low order and requires such rigid control that a clean separation is a matter of some difficulty. Here might be pointed out the extreme importance of ensuring that the supplies of barytes conform rigidly to the specification for fineness. Any increase in coarseness will increase the barytes loss in the sand spigot.

As a result of the differential settling ratio, a certain proportion of the fine-grained sand has equal settling with the coarser grains of the barytes. Thus barytes which will just pass a 300-mesh screen has a diameter of 0·0425 mm. With a settling ratio of 1·19 these grains will be equal settling with a quartz grain of $0{\cdot}0425 \times 1{\cdot}19$ mm. or 0·0506 mm. diameter. Thus, it is impossible to separate quartz grains of this diameter (250 mesh) or smaller from 300-mesh barytes under the best ideal conditions. Allowing for minor variations in feed and occasional crowding of the grains in

the sorting column, with a consequent change to hindered settling ratios, it is evident that the figures of ideal performance will not be attained.

With regard to the barytes concentration from the clay, this is a simple matter in the case of the coarser barytes grains. Extending the argument as to the decrease in settling ratio with decrease in grain sizes, however, it follows that for very minute grains they will be equal settling whatever the differential of gravity. The ground barytes will contain a certain proportion of these fine grains, and it therefore follows that they will be lost in the overflow. It would be quite uneconomical to reduce rates of feed to ensure the settling of these very fine grains.

Hydraulic Classification.

In simple language mineral classification is effected by imparting to the diluted mud a carrying current either vertical or horizontal in direction. Provided that this current velocity is greater than that of the settling velocity of any grain, such grain will be carried by it. If, however, the settling velocity of any grain exceeds the current velocity, it will sink.

The velocities requisite to ensure the sand settling and the barytes rising are best obtained by an elutriator or small-scale tubular classifier. As the velocities are of a low order, the hydraulic water must be at constant head, to ensure constancy of the rising velocity during the duration of the test. While the velocities obtained are not always directly applicable to diluted mud, they do give an insight into the extent of separation possible, and are a valuable means of checking the barytes specification. In a like manner, the velocity necessary to ensure settling of the barytes can also be determined.

These tests indicate a rising velocity of 3·5–4·0 mm./sec. for the barytes–sand separation and of 1 mm./sec. for the settlement of barytes. In larger scale tests with a complete model plant treating diluted mud, the respective velocities were found to have average values of 3·5 mm./sec. and 0·6 mm./sec.

The main point to be noticed is that very slight variations in these velocities will result either in more sand floating or more barytes settling. Thus absolute constancy of feed is an essential especially if the process is to be continuous.

Classifiers may be divided into two main groups:

1. Those using hydraulic water.
2. Those not using hydraulic water.

1. *Using Hydraulic Water.*—In these the rate of feed is adjusted according to the requisite velocity, and hydraulic water is fed in at the bottom. Thus, sinking grains are subjected to an upward-rising current. If heavy enough to settle through this current, they may do so, and are discharged at the spigot. In ore dressing, the hydraulic classification of grains smaller than 0·1 mm. is not attempted. The sand grains in mud are often much smaller than this, but the fact that we are dealing with suspensions much more highly charged with solids than is the case in most mills, and that there is a double sorting action, first by the rate of feed and secondly

by the hydraulic water, appears to favour the choice of such a classifier for the barytes sand separation.

2. *Not Using Hydraulic Water.*—These are more particularly applicable to the separation of fine-grained material from slimes, and therefore for the separation of barytes from clay. In such separation the requisite velocity to allow of the barytes sinking is of such a low order that it calls for far too accurate an adjustment of hydraulic water, or, if the lower sorting column is made large enough, of far too big a consumption of water for the hydraulic feed. Thus, in such cases separation is best effected by direct settling in water.

Considerations as to Selection of Plant.

The following notes are more applicable to small fields such as we have in Trinidad. In the opening remarks it was indicated that sand separation and thickening, or, it might now be added, a more ambitious classification in series, would probably be preferable for large-scale operators.

The capacity of the plant will naturally vary from field to field, being governed to a large extent by the barytes consumption and the dilution required.

The conclusions so far arrived at might now be summarised:

1. Free settling is preferable to hindered settling, so dilutions should be such as to ensure that the individual grains are free settling.
2. The rates of feed must be very carefully regulated, and must be absolutely constant.
3. A classifier using hydraulic water is preferable for the barytes sand separation.
4. A classifier with no hydraulic water is preferable for barytes clay separation.

To these might be added the fact that the feed must be relatively free from oil. Sand grains coated with oil have settling rates quite other than clean grains, and apart from this there is some evidence that free oil has a flotation effect, especially in the barytes clay separation. In most cases adequate mixing during dilution will ensure the release of such oil, but when treating mud from old slush pits, steam coil heating may also be required.

The Author is strongly in favour of gravitational feed throughout the treatment. Quite apart from its cheapness, it permits of a very nice control of the rate of feed, if under constant head conditions, and the feed will be steady. With mechanical feeds there is a danger of pulsations, and also of fluctuations with steam or other power variations.

The water added during dilution must be intimately mixed with the mud, and some means must be provided to ensure that the barytes and sand remain in suspension and do not settle in the dilution tank. If the diluted mixture is not intimately mixed, or if settling out of the heavy grains occurs, the percentage of solids in the feed to the classifier is liable to wide fluctuations. This may well set up hindered settling conditions or, what is more likely, will cause clogging of the sand spigot. The Author

has had good results in a model installation with a conical mixing tank for the water and mud.

The question now arises as to whether the treatment should be by batches or continuous. If batch treatment is selected, it allows of less rigid control of rates of feed, as recycling can be carried out. It may also permit of slightly lower dilution ratios. The Author is, however, in favour of continuous treatment, with continuous draw off of sand and barytes from their respective spigots. This entails very careful calculation of the relative settling areas of the two classifiers to ensure the correct velocities in each, but is preferable by virtue of the increased throughput and constancy of the recovered product.

The question of drying out of the recovered barytes, or of mixing it in sludge condition, is largely governed by the location of the recovery plant. If located at a central mud plant provided with a duplicate system of mud lines to the drilling wells, the writer is not in favour of drying and bagging, owing to the extra cost entailed. If all mixing is carried out at the well, such a procedure must be adopted.

With regard to the design of the hydraulic classifier for the sand separation, it must be remembered that the classification to be carried out is on fine grains. A deep pocket, as opposed to a shallow pocket classifier, is therefore indicated. This will give individual grains a longer time for settling or rising, and will promote a finer sorting. In order to have uniform velocity conditions in the rising current, a straight-sided upper sorting chamber is indicated. The writer favours also a long lower sorting column up which the hydraulic water rises somewhat on the lines of a tubular classifier.

The diameter of this sorting column is rather dependent on the quantity of sand in the feed, and to some extent on the fineness of the individual grains. It is obvious that if the sand content in this column becomes too high, choking of the spigot may result. It is safer to make it of such a diameter that with the maximum amount of sand to be expected in a mud, the proportion of sand to water in it does not exceed 1 : 5.

Having calculated the diameter of the sorting column, the volume of wash water must be adjusted, with the spigot open, so that the upward velocity in the sorting column is equal to that of the upward velocity in the sorting chamber induced by the rate of mud feed. This will inhibit banking at the point where the two streams meet. Actually the rate of feed of hydraulic water should be reduced to allow for the sand in the sorting column, as this sand will decrease the volume of the column, and therefore increase the upward velocity. Actually also the rate of mud feed should be reduced by the amount of hydraulic water. This, of course, can be allowed for, but in practice the hydraulic water is such a small fraction of the total feed that it can be neglected. If the sand content is high, or if there is a large proportion of fine grains in the sand, a relatively large sorting column may be required, and in such cases allowance for the hydraulic water must be made. It is preferable to give the wash water a whirling motion up the sorting column, which will ensure a constant rising velocity distributed over the whole cross-sectional area of the sorting column, and thus inhibit the formation of inversion or downward currents.

The diameter of the spigot discharge must be capable of dealing with the sand content of the mud being treated. If too small, the sand will accumulate and choke the spigot; if too large, much water will be wasted. The Author's experiments indicate that a concentration of 1 part of sand to 5 parts of water can be discharged continuously without clogging. If the spigot size is altered, the hydraulic water will need adjustment. The minimum size of spigot is about three times the diameter of the maximum size of grain to be settled.

It is not proposed to enlarge upon the type of classifier best suited for barytes separation from the clay mud. It must be of such a size that the velocity of flow when fed with the overflow from the hydraulic classifier is slow enough to settle the barytes (about 0·5 mm./sec.). Means must be provided for drawing off the settled barytes, and also for collecting the overflow. The Author is personally in favour of a conical classifier with central feed and peripheral overflow, as this allows for simple discharge of the barytes from a spigot situated at the apex of the cone. He has found that relatively thick sludges can be continuously discharged from the spigot of such cones and may be simply unwatered in a small whole-current settling-box. It would also be advisable to pass the overflow from the cone through a whole-current settling-box to settle any barytes that has passed over. If preferred, the spigot may be replaced by a gate and the barytes drawn off intermittently, in which case a thicker product will be obtained.

The only other item that requires careful attention is the design and slope of the launders for the mud feed to the hydraulic classifier and to the second classifier. If too wide, or placed at too gentle a slope, sand and barytes will settle in them, and they will become clogged. If placed at too steep a slope, or of too narrow a width, the high velocities will cause a plunging current into the classifiers, which may entirely upset the quiet steady currents so essential to good classification.

The question of the results that can be expected from a barytes recovery plant is approached with some diffidence. The figures in this paper are based on a model laboratory plant, which, whilst complete in all details, may not represent full-scale performance. (Fig. 1 is a diagrammatic sketch of a small plant now in course of erection. It is identical with the laboratory model except for minor changes in the sand classifier design.) It is felt, however, that the larger volumes to be dealt with in practice will allow of more latitude, and that these figures may be regarded as a minimum.

In practice, it may not prove economical to carry out separation to its optimum. For instance, operators may find, owing to shortage of water, that it is preferable to cut down the dilution below its optimum value, even at the expense of a lower specific gravity and yield of barytes. While the Author has found in some cases that a dilution of 10 parts of water to 1 part of mud is indicated, in others quite good results have been obtained with dilutions of 7 : 1.

The average loss of barytes in the sand spigot is about 10–15 per cent., but as barytes has been used which is considerably off the specification for fineness, this figure is liable to be a maximum. The hydraulic water in a model plant is so small in volume that it is very difficult to maintain a

close adjustment. Naturally, this loss can be greatly decreased by increasing the rates of feed, but only at the expense of a decrease in the specific gravity of the recovered barytes. It has been indicated earlier that some barytes must be lost in the hydraulic classifier spigot, or, alternatively, there will be an increase of sand in the barytes. The most economic balance must be struck. The loss in the hydraulic spigot could probably be reduced by either a two-stage sand classification, or by recycling. It is questionable whether either would prove as economical.

It has also been shown that 250-mesh sand or smaller cannot be separated from the larger barytes grains. It is therefore quite impossible to obtain a barytes with a specific gravity equivalent to that of the original product without excessive loss in the sand spigot. Apart from this very fine sand contamination there is some contamination by the clay portion of

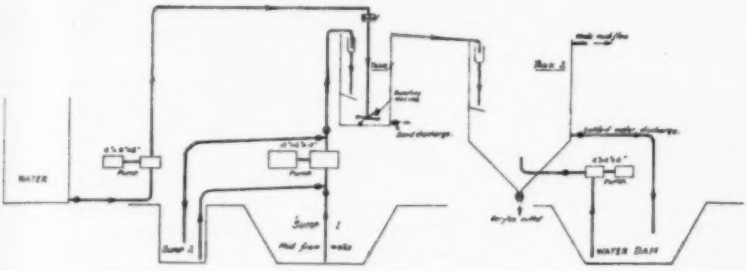

FIG. 1.

CYCLE OF OPERATION :—

1. 28 Bbls. of mud from wells is pumped into Sump 2 from Sump 1, and mixed with equal quantity of water.
2. The diluted mud in Sump 2 is pumped into Tank 1 (which is full of water).
3. Simultaneously 60 Bbls. of water is pumped into Tank 1 through the rotating ¼" nozzles.
4. The sand and cuttings settle in Tank 1 and the shale and barytes are carried over into Tank 2 against an upward current of water in Tank 2, adjusted so that the shale is carried up to overflow, and the barytes allowed to settle. Washing is continued until the overflow is clear.
5. Settled barytes is drawn off from the bottom of cone, washed into preliminary drying pans, where oil is skimmed and water drawn off, finally dried on open coils, rolled and bagged.

the mud. It appears that the grains of barytes are coated with extremely thin layers of the gel-forming colloids of the mud. This somewhat reduces the rate of settling and the resultant specific gravity. The evidence for this phenomenon is the increased difficulty of wetting of the recovered barytes and a slight tendency to froth and remain in suspension. Naturally, this will be beneficial rather than detrimental for subsequent mud-mixing purposes. As a result of this sand and clay contamination, the Author's tests indicate that specific gravities better than 3·97 cannot be anticipated. If, however, the fine-sand content of the muds is lower, or if the clay is non-colloidal, this figure may be increased in other fields.

The amount of barytes passing into the cone overflow is largely dependent on the dilution, and it is in this stage of separation that adequate dilution is so important. Naturally, the settling area can be so increased as to

allow for the settling of almost all the barytes, but again this will probably prove uneconomical. Total extraction of the barytes in this classifier without undue clay contamination is virtually impossible, as the minute grains are equal settling, irrespective of the differentials of gravity.

DISCUSSION.

Mr. H. C. H. Thomas. The Author had stated that water consumption was important from the point of view of cost. Once barytes had been recovered, clarification of the water could be accelerated by addition of electrolytes—that is to say, that the colloids could be precipitated from the water and the water used again. The speaker suggested that if in the first stage the dilution water contained electrolytes, the colloidal properties of the mud would be destroyed before it went through the process, and would therefore decrease the amount of dilution necessary and increase the rate of settling.

With reference to centrifuging, he quoted the Author's statement, and gave data that he had collected on the point. He suggested that a sand classifier would be advantageous if it did not seriously affect the transportability of a centrifuge. He did not consider it a necessity, however, as the only movements of sand grains in the bowl of the centrifuge would be: (*a*) settling; (*b*) overflow; (*c*) slippage, which could be reduced by baffles. The sand would not, therefore, have very considerable abrasive effect. He invited the Author's views on those points.

Mr. H. D. Fletcher inquired whether it was essential to separate barytes from the mud. His experience was that if the sand and gas could be removed, the remaining mud was suitable for drilling with, and barytes could be added to it to increase the weight if necessary. He thought that as the separation of the barytes from the mud was the most costly part of the process, its elimination would be a considerable saving of time and money. The removal of sand and gas only would require less water, take less time, and the plant would be less costly.

Mr. A. J. Ruthven-Murray said that they had a small barytes recovery plant (Fig. 2) which was operated on the batch principle for barytes separation, and that it worked very satisfactorily, treating 28 barrels of mud at a time, this having an average weight of 92 lb. Although 100–110 lb. mud was generally used on the field, the mud treated was down to that weight because a certain amount was stored in dams into which had been pumped for many years both barytes-laden and plain shale mud, thus diluting the barytes content of the mud and lightening it. However, they ran a batch of 28 barrels at a time having an average weight of 92 lb., and recovered 1600 lb. of barytes from each run. Two batches were washed during the daylight period of 8 hours, and the drying process took from 16 to 20 hours.

It was intended to add additional drying coils, so that with the same size of plant three times the amount of barytes could be recovered. For every 56 barrels of mud treated approximately 1½ tons of barytes was

recovered. The cost for this operation was $15.00 all in—fuel and labour—and they recover a minimum of $30.00 worth of barytes. By installing additional drying coils it was calculated that 4½ tons of barytes would be recovered for an all-in cost of $25.00. He expected that later on, when the poor surface mud had been worked over, they would obtain a higher concentration of barytes in the settled mud in the dam, and so would find the costs go down by virtue of a large quantity recovered.

With regard to Mr. Fletcher's question, the speaker had mentioned at a previous meeting dealing with mud, that in the Parry Lands area an excess of shale mud was made in the wells. When drilling, mud had constantly to be pumped away, either to mud dams or into the river.

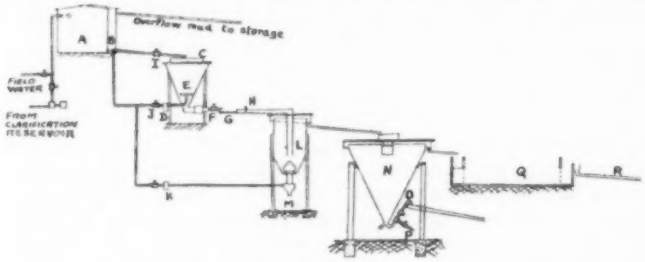

FIG. 2.

A. Water Tank (Constant fluid level maintained by a ball valve).
B. Mud Tank (Mud only diluted to give free-flowing characteristics).
C. Coarse screen for removal of cuttings from mud.
D. Flow indicator for regulation of dilution water.
E. Dilution cone (Mud and water intimately mixed by counter current flows). Fluid level maintained constant by regulation of valve I with correct setting of Valves F and J.
G. Fine screen for removal of fine cuttings.
H. Wall for skimming of oil from mud.
K. Flow indicator for regulation of hydraulic water.
L. Hydraulic classifier for barytes–sand separation.
M. Sand spigot discharge.
N. Barytes–clay surface current classifier.
O. Discharge of barytes pulp to mixing plant.
P. Valve for water injection in case of blockage of spigot.
Q. Whole current settling box for removal of any barytes in overflow. Only cleaned periodically.
R. Overflow water to clarification reservoir.

In the latter case, barytes mud would be lost, and so the best method was to recover the barytes from all spare mud, sack it, and use it again, simply throwing away the shale portion.

It might interest Members to know their method of operation. The mud was first mixed in the dam with guns, and then pumped up into a suction box, where it was diluted in the proportion of 2 parts of water to 1 part of mud. It then went into the first tank, where it was washed in a similar manner to that described by Mr. Scott, *i.e.* the mud was pumped up from the suction pit and down through a pipe into the bottom of the tank 4 ft. in diameter and 9 ft. high. In the centre of the tank was a 2-in. tube carried on a swivel with two cross-arms on the bottom, each cross-arm carrying a jet at each end, set at right angles to the arm

and tilted upwards at a slight angle. The water was pumped down this centre tube, and the pump pressure caused the jets to rotate, thereby distributing the water through the mud mixture and creating sufficient agitation to prevent the shale and barytes from settling before being caught up in the rising current. The volume of washing water pumped down was equal to the volume of diluted mud in the suction pit; so that there was actually a dilution of 5 of water to 1 of mud in the de-sanding tank. The sand then settled to the bottom of this tank, whilst the barytes shale mud flowed over into the next tank, 9 ft. in diameter and 9 ft. high, with a conical spigot at the base. Washing water was then pumped into this second tank at a point near to the bottom, and circulation took place for an hour to wash the mud, the speed of the upward flow being so adjusted that the shale was carried upwards and the barytes allowed to settle. During that hour 80 barrels of water were pumped in, and at the end of the hour it was found that the water came over quite clear and, as already explained, the barytes recovered in one batch was 1600 lb. Their plant was installed on the slope of a hill so as to ensure gravity feeds at all stages and minimise handling. The barytes recovered from the spigot was then washed down a concrete ditch into an iron drying-pan; sometimes the concentrate carried a film of oil, and in this case the whole batch was heated with plenty of water, so that oil came to the surface and was flowed off together with any excess of water. The barytes concentrate was then dried by steam coils until reduced to a plastic state, when it was shovelled up and distributed upon a series of steam coils lying flat on a concrete platform. During the process of drying, the barytes was turned slightly by men with shovels. The barytes was dried completely on the steam coils, and in doing so was reduced to powder. The few lumps which remain fell to powder immediately they were touched, and for this purpose a light roller 8 ft. long, made of 6-in. casing, was used for pressing out the barytes before it was sacked. It was then stacked in a shed on the lower side of the hill, from which trucks took delivery of barytes for transport direct to the well. They only drew on their main barytes storage at the jetty when the stock of recovered barytes was exhausted.

Mr. J. L. Harris said that the Author mentioned that he obtained 80–85 per cent. recovery of barytes from his plant. He was very anxious to know what his view was as to the total recovery of barytes from the quantity used in a well. Mr. Scott's experiments, of course, did not show what percentage of the barytes originally purchased arrived at the plant for recovery. Economically, the essential figure was the number of tons of barytes eventually recovered at the plant from each 1000 tons placed in the well.

Mr. L. K. White inquired about the suitability of sea-water or well-water for mud treatment. He said in some places the scarcity of water had been the breaking-down point in recovery plants, whilst if sea-water was suitable, it might be available, and in some places well-water was available. Would it be suitable for dilution in the first instance?

He also requested Mr. Ruthven-Murray to give him some indication of

the salvage of water that was used in the recovery of the barytes from the 28 barrels.

Mr. Ruthven-Murray stated that the actual quantity of water used was 220 barrels for 28 barrels of mud, which represented a dilution of 8·6 : 1. Mr. Scott referred to a maximum dilution of 10 : 1 and a minimum of 7 : 1. So far no water has been salvaged, but a dam for this purpose was being made.

Mr. A. Frank Dabell said that, as a precautionary measure, the successful recovery of barytes appeared to be a matter of urgency, but for so long as barytes could be delivered to the well at £5 per ton but little margin remained for its application. This no doubt accounted for the abandonment of the many installations of the past few years.

Whilst conceding full credit for the method described that evening of recovering barytes in a dry form, it appeared to him in all reason that more promise lay in recovery in liquid form.

Mr. G. H. Scott, in reply, said that Mr. Thomas had raised the point whether settling rates could not be accelerated and dilutions reduced by the addition of electrolytes prior to classification. Coagulation by electrolyte addition induced coalescence of the particles, so that settling rates calculated on individual grains would be liable to be completely upset. Furthermore, the flocculent nature of the coagulum was liable to cause choking of the spigots. He considered that electrolyte addition at this stage would be detrimental to a clean classification.

With regard to the centrifuge, he would defer to Mr. Thomas on the point of wear of the bowl, as he had had no experience of the separation of sharp sand from clay suspensions by means of centrifugal force. He would have imagined, however, that abrasion and wear were bound to occur, especially in centrifuges, where provision was made for constant discharge of the coarse-grained material.

Mr. Thomas appeared to favour the centrifuge by virtue of its portability. This was an undoubted advantage. He still felt, however, that the ideal location for a barytes recovery unit was at a central mud plant. When so located the set-up would be of a semi-permanent nature, and there was little or no advantage in portability. In cases where such mud farms did not exist, it must be borne in mind that a machine running at 600 r.p.m. required massive foundations, and arrangements would have to be made for feed and collection of the products. Thus the cost of erection at varying locations would be a serious item, and would decrease the ultimate profit.

Mr. Fletcher asked whether it would not be preferable to de-sand only, merely reloading the overflow mud with barytes. The Author had attempted to show that such a programme would be justifiable perhaps in the case of a large-scale operator and when good quality clay for mud-mixing purposes was at a premium. In Trinidad, 90 per cent. of the fields had no shortage of clay—in fact, the converse was more generally the case. After a dilution varying from 7 to 10 parts of water per part of mud, the barytes–clay suspension must be thickened to almost its

initial specific gravity, in order for the process to be economical; otherwise much barytes would have to be added to restore weight. The area of the thickener then became so great that its installation would be justifiable only in cases where large-scale drilling operations could guarantee a constant supply of mud for reconditioning.

Mr. Ruthven-Murray's remarks were of peculiar interest, in that they showed the profitability of a barytes recovery scheme even when carried out on a comparatively small scale. With regard to the possible effect of water clarified by alum, if the alum addition was calculated correctly, most of this electrolyte sank with the coagulum, and there was little change in the *p*H value after treatment. If, however, it was found to have a slight flocculating effect, this water could always be used for boiler-feed purposes, and the requisite volume for the recovery unit made up from the field supply.

He thought Mr. Harris's point a very good one.

Assuming a recovery of 80 per cent. of the barytes in the mud treated, it was obvious that such a figure could not be applied as indicative of the percentage of the total consumption that would be recovered. Loss into the formations traversed and the quantities left behind casing were such that any operator must consider himself lucky to recover 50 per cent. of the total consumed.

Mr. White asked about the feasibility of using sea-water in place of fresh water for dilution purposes. While the Author had not experimented with salt water, he considered that, at the worst, such water would have only a minor flocculating effect and should not greatly affect classification. The relative velocities of settling would naturally be changed slightly owing to the slight increase in specific gravity of the water.

The Chairman questioned the economy of barytes recovery with the product standing at £5 per ton. The Author felt that a fair margin of profit would still accrue to the operator of a carefully designed plant even at that figure, and had received corroboration from Mr. Ruthven-Murray, whose figures were based on actual operation. The Author stressed the fact that quite apart from the direct benefits of barytes recovery, there were the indirect ones of reduced wear on drilling plant as a result of sand removal and the increased drilling speed resultant on changing the mud immediately it had deteriorated to an extent sufficient to hinder progress. It was difficult to assess the actual value of such indirect benefits, but they must be taken into account in all calculations as to the profitability of such a plant.

On the motion of the Chairman, a vote of thanks was accorded to the Author, and to their Hosts, the President and Members of the Apex Club, for the use of the building.

A CONTRIBUTION TO THE STUDY OF OIL-FIELD WATER ANALYSIS.

By Wilfred Richard Wiggins, B.Sc., and
Charles Edmund Wood, M.Sc., A.I.C. (Member).

PART IV.

Estimation of Sodium by Means of Zinc Uranyl Acetate.*

SYNOPSIS.

1. Previous investigators using the double magnesium, zinc, nickel, or cobalt uranyl acetates have suggested various procedures whereby sodium is determined gravimetrically, colorimetrically, or volumetrically. The present Authors have developed the method into an accurate and convenient volumetric method for the determination of sodium.

2. The sodium salt precipitated by zinc uranyl acetate under specified conditions of concentration and temperature was analysed, and found to have a constant composition corresponding with $NaZn(UO_2)_3(CH_3{\cdot}CO_2)_9\,6$ or $6\frac{1}{2}H_2O$. Precise knowledge of the number of molecules of water of crystallisation in the salt is not necessary for the volumetric determination.

3. The solubility of the salt increases only slightly with temperature within the limits investigated, namely, 5–25° C. For normal laboratory practice, 15° C. is a convenient temperature to employ.

4. The precipitated sodium salt was estimated after elimination of the acetyl radical by reduction of hexavalent uranium in the salt to the tetravalent state, the solution then being titrated with 0·1*N*-potassium permanganate.

5. Precipitation of the salt is for all practical purposes complete after 1 hr. The whole estimation for sodium takes approximately 3 hrs.

6. Sodium can be estimated in concentration corresponding to 2·5–40 grs. NaCl per litre. For concentrations corresponding to 2·5–5 grs. NaCl per litre, the reaction volume of 35 ml. containing 25 ml. reagent should be employed; for concentrations corresponding to 5–40 grs. NaCl per litre, the reaction volume of 105 ml. containing 85 ml. reagent is an appropriate quantity.

7. Potassium has no appreciable effect in concentrations corresponding to less than 37·5 grs. KCl per litre.

8. The ammonium radical causes a negative error proportional to its concentration. The error becomes high with concentrations greater than 25 grs. NH_4Cl per litre.

9. The magnesium ion alone causes a slight negative error, and magnesium in the presence of ammonium results in a large negative error, increasing as the concentrations of magnesium and ammonium increase.

10. The effect of calcium alone and in the presence of ammonium is similar to that of magnesium under the same conditions.

The previous paper [1] in this series of contributions detailed a method for the direct estimation of sodium using dihydroxytartaric acid. Although the method is accurate, it was necessary to carry out the determination at 5° C., to allow the precipitating solution to stand 5 hrs., and to apply an appreciable solubility correction. On account of these factors it was decided to investigate the use of a double uranyl acetate as the precipitating reagent for sodium.

* Paper received March 14th, 1934.

Oil-field waters generally contain Na, and in addition K, Mg, Ca, and sometimes NH_4 ions; it is therefore necessary in the determination of sodium in oil-field waters to examine the effect of these ions on the estimation. Also, to render the method suitable for routine work, it is desirable to investigate the time necessary for complete precipitation, to specify a definite reaction volume, and to determine the errors obtained at various concentrations.

The method was first suggested by Streng,[2] who described magnesium uranyl acetate as a qualitative precipitating reagent for sodium, and, in addition, the zinc, cobalt, nickel, iron, and manganese compounds.

Only in recent years has this work been developed; and these developments can be traced by reference to the bibliography given at the end of the paper.

Composition of the Triple Acetate.

All investigators agree that the salt contains water of crystallisation, $NaZn_3(UO_2)_3(CH_3{\cdot}CO_2)_9{,}xH_2O$, but there is lack of uniformity in the figures given for the number of molecules of water present.

The degree of hydration is immaterial in volumetric determination, and also in the determination of uranium gravimetrically, since the ratio of the component radicals only is considered; it is, however, important should the determination of the amount of triple salt be made gravimetrically. It was desirable to ascertain whether the formula $NaZn(UO_2)_3(CH_3{\cdot}CO_2)_9$ assigned to the salt represented its actual composition, and to determine the number of molecules of water present.

Preparation of Zinc Uranyl Acetate, the Precipitating Reagent.—The reagent was prepared by the method given by Dobbins and Byrd, two solutions being made up as follows:

Solution A.		Solution B.	
Uranyl acetate, A. R. . .	85 gr.	Zinc acetate, A. R. . .	200 gr.
Acetic acid glacial, 98 per cent.	50 ml.	Acetic acid glacial, 98 per cent.	25 ml.
Distilled water . . .	400 ml.	Distilled water . . .	250 ml.

In order to dissolve the solids, each solution was heated to 70–75°, then mixed, cooled, and filtered. This is the concentration of the reagent used throughout the series of experiments described in this paper.

Preparation of Sodium Zinc Uranyl Acetate.—250 ml. of the above reagent were added to 25 ml. of sodium chloride solution (conc. 25 gr. per litre). These quantities were chosen so that the triple acetate would be precipitated in the usual concentration approximately for sodium estimation. The mixture was allowed to stand at 5° C. for 24 hrs., filtered under suction, and the crystals were washed with absolute alcohol and allowed to dry on a filter paper in the atmosphere.

Analysis of the Triple Salt. Estimation of Sodium.—This was carried out by the dihydroxytartaric acid method developed in Part III. Uranium and zinc were precipitated by ammonium sulphide in the presence of ammonium chloride, this precipitation being repeated and sodium estimated in the combined filtrates, which were evaporated down with sulphuric acid to give the desired sodium concentration.

Estimation of Zinc.—For this purpose, the 8-hydroxyquinoline method of Berg [3] was chosen. The precipitation of the brown uranium hydroxyquinolate was prevented by carrying out the precipitation in (*a*) slightly

acid tartrate medium, (*b*) slightly alkaline malate medium, the excess of 8-hydroxyquinoline being kept within narrow limits.

Experiments carried out with a solution of zinc sulphate and with a synthetic mixture of zinc sulphate and uranyl acetate having a similar $\frac{U}{Zn}$ ratio to that of the triple salt indicated that the method of analysis (using 8-hydroxyquinoline in an alkaline tartrate medium) had an inherent error ranging from 0·129 to 0·4 per cent. Applying these corrections to the average value obtained for zinc in the triple salt gives a value ranging between 4·22 and 4·23 per cent. for zinc.

Estimation of Uranium.—The Jones Reductor [4] was used. Reduction of hexavalent uranium proceeds partly to the tetravalent and partly to the trivalent stage, trivalent uranium being re-oxidised to the tetravalent stage by bubbling air through the solution. These changes in valency are accompanied by corresponding colour changes: uranyl salts, bright yellow-green; trivalent uranium salts, dark green; tetravalent uranous salts, pale sea-green. On titration with potassium permanganate the end-point is taken when the solution assumes a faint pink tint, and this end-point is corrected by means of a solution of a ferrous salt and ammonium persulphate.[5] It was found that in the presence of uranium, acetates are reduced by this process, and therefore it is necessary to eliminate them by warming with 60 per cent. H_2SO_4 on a sand-bath for about 1 hr. until fumes are evolved.

Estimation of Acetate Radical.—Perkin's acetyl method was used. Modifications adopted were the use of phosphoric instead of sulphuric acid, carbonate free potassium hydroxide and a two-bulb splash head with condenser attached to receiver limb.

From the above analyses, the following conclusions were reached: (1) the sodium salt precipitated under the conditions given above is of constant composition, different samples obtained at different times when analysed gave identical percentage values for the constituent radicals; (2) the compound corresponds to the empirical formula $NaZn(UO_2)_3(CH_3{\cdot}CO_2)_9,xH_2O$; (3) the number of molecules of water in the compound is either 6 or 6½.

The difference in the percentage values for Na, Zn, U, and acetyl radical calculated for 6 or 6½ molecules of water is so small that it is well within the limits of experimental error which the following table (Table I) indicates.

TABLE I.

	Na.	Zn.	U.	CH_3CO_2.
Experimental results expressed as percentages.	1·483	4·1992 } using	46·18	33·95
	1·489	4·1995 } tartrate	46·11	34·43
	Average	4·2455 } medium.	46·02	34·24
	1·486	4·2074	Average	34·69
		Average 4·2129	46·10	Average
		Applying solubility correction.		34·33
		Average 4·22 to 4·23		
		4·245 using alkaline malate medium.		
Calculated for $NaZn(UO_2)_3(CH_3CO_2)_9,xH_2O$.				
$x = 6$	1·495	4·251	46·45	34·54
$x = 6\frac{1}{2}$	1·486	4·226	46·17	34·34

Solubility of the Triple Salt.

The solubility of the salt was determined at various temperatures by the method indicated by Findlay,[6] the salt and solution being shielded from the decomposing effect of direct sunlight. The results given in Table II show that there is no appreciable increase in solubility from 5° to 15° C., and thus there was no necessity to conduct the experiments at the lower temperature.

The triple salt is appreciably soluble in water at ordinary temperatures—namely, 5–6 per cent. Quantitative precipitation depends on an excess of the zinc uranyl acetate being present which depresses the solubility to a negligible amount.

Table II.

Temperature (° C.)	5	10	15	20	25
Solubility, grs. salt per 100 c.c. water	5·015	5·428	5·586	5·879	6·298

Volumetric Method for the Estimation of Sodium.

Discussion.—The complex nature of the salt and its constancy of composition afford a wide choice for the determination of sodium volumetrically, it being necessary merely to precipitate the salt, filter and determine the amount of zinc, uranium, or acetyl group present by the methods described in the analyses. The estimation of zinc by 8-hydroxyquinoline using an alkaline malate medium is a simple procedure, but the percentage of zinc in the salt is only 4·23, and $\frac{Zn}{Na}$ weight ratio is less than 3. The weight ratio, however, of $\frac{acetyl}{Na}$ is more favourable, being just over 22, but the method possesses inherent errors due to the effect of atmospheric carbon dioxide, acidity of the alcohol, and blank tests are necessary. The estimation of uranium requires simple apparatus, easily obtainable and stable reagents; further, the weight ratio $\frac{U}{Na}$ is most favourable, being 30·7. This last method was, therefore, adopted.

Method of Precipitation.—Three reaction volumes were used in the experiments:

(1) 5 ml. sodium chloride solution of different concentrations, 25 ml. reagent solution, water to 35 ml. (*i.e.*, 5 ml. water added).
(2) 5 ml. sodium chloride solution of different concentrations, 50 ml. reagent solution, water to 70 ml. (*i.e.*, 15 ml. water added).
(3) 5 ml. sodium chloride solution of different concentrations, 85 ml. reagent solution, water to 105 ml. (*i.e.*, 15 ml. water added).

The water was added to the sodium chloride solution in small beakers of appropriate size, then the reagent was added while stirring. The mixture was put in a constant-temperature bath at 15° C. for a stated time (usually 1 hr.), the precipitate was filtered under suction in a Gooch crucible—porosity B1 or B2—well drained, and then washed with absolute alcohol

TABLE III.

Influence of Time of Standing on Precipitation.

NaCl, grs./litre	5·0341	5·0341	5·0341	5·0341	5·0341	5·0341	5·0341	5·0341
Time of standing (hrs.)	½	¼	1	1	2½	2½	27½	27½
Temperature of precipitation (° C.)	15°	15°	15°	15°	15°	15°	15°	15°
$KMnO_4$ required	23·95	23·96	24·29	24·53	24·37	25·10	25·32	25·33
Na found (grs.)	0·0096992	0·0097033	0·0098369	0·0099422	0·0098693	0·0101649	0·0102540	0·0102580
Na present (grs.)	0·0099224	0·0099224	0·0099224	0·0099224	0·0099224	0·0099224	0·0099224	0·0099224
Error	−0·0002232	−0·0002191	−0·0000855	+0·0000198	−0·0000531	+0·0002425	+0·0003316	+0·0003356
Error per cent.	−2·25	−2·21	−0·86	+0·20	−0·53	+2·44	+3·34	+3·38
Average error per cent.	−2·23		−0·33		+0·95		+3·36	

$KMnO_4$, 0·10566*N*.

saturated with the triple acetate. The crucible containing the salt was placed in an evaporating dish with 5 ml. 60 per cent. sulphuric acid and the whole warmed on a sand-bath for 1 hr. until no odour of acetic acid was discernible and fumes of sulphuric acid were evolved. The residual liquid was washed into the reductor with 50 ml. water. An additional 50 ml. of water were used for freeing the evaporating dish, crucible, and reductor from any traces of uranyl salt. After passage through the reductor, bubbling air for 10–15 minutes was sufficient to convert the dark-green trivalent uranium solution to the stable tetravalent stage. The solution was titrated with $N/10$-potassium permanganate solution to a permanent pink coloration. An end-point correction is necessary for the excess potassium permanganate which is required to give a discernible pink colour in a green solution; 1–2 drops ferrous salt solution are added to decolorise the excess permanganate, then 0·2–0·5 gr. ammonium persulphate are added to oxidise any excess ferrous salt, and the solution is titrated until the original pink colour was obtained. The correction is the amount of potassium permanganate necessary to restore the solution to its original colour. (1 Na = 3 U in compound. $\frac{U}{20} = 1000$ ml. 0·1N-$KMnO_4$ solution. 1 Na = 60×1000 ml. 0·1N-$KMnO_4$. $\frac{23}{60 \times 1000}$ gr. Na = 1 ml. 0·1N-$KMnO_4$.)

Influence of Time of Standing on Precipitation.—Table III shows that (*a*) half an hour is not sufficient for complete precipitation, (*b*) the occlusion error overwhelms the error due to non-precipitation on standing for a long time (27½ hrs.), (*c*) errors due to occlusion and non-precipitation tend to balance each other after standing for 1 hr., (*d*) experiments were carried out with low sodium chloride concentration in order to apply a severe test to the method.

From the evidence supplied by these tests a minimum time of standing of 1 hr. was allowed for all experiments, and in most cases for confirmation of our results experiments were also carried out after standing for either 2¾ or 24 hrs. (Cf. Tables IV and V.)

Relationship of Concentration and Reaction Volume.—Throughout the work, all experiments were carried out in duplicate as a minimum. The first reaction volume used was 35 ml.; with this the method failed for concentrations of less than 2·517 grs. sodium chloride per litre, this being too dilute for estimation, and for concentrations greater than 10·1373 grs. per litre, owing to insufficiency of excess of the precipitating reagent, viz., zinc uranyl acetate solution. Unless an excess of reagent is present, the triple salt is soluble. Between these two concentrations the method is most satisfactory. (Refer to curve 1, Diagram 1.)

The second reaction volume used was 70 ml. between sodium chloride concentration limits of 10·1373 and 40·0267. At the lower concentration the method failed as before owing to dilution; and at the higher on account of lack of excess of precipitating reagent. The results Table IV and Diagram 1, curve 2, show that at intermediate concentrations the method always gives a negative, though not large error, therefore a third reaction volume of 105 ml. was employed. Using this, the method was satisfactory through a wide range of concentration—namely, 5–40 grs. NaCl per litre.

TABLE IV.

Influence of Concentration and Reaction Volume on Sodium Determination.

Reaction volume (ml.)	35	35	35	35	35	70	70	70	70	105	105	105	105
NaCl (grs./litre)	1·2585	2·5170	5·0341	10·1373	19·8439	10·1373	19·8439	30·0625	40·0267	5·0341	10·1373	19·8439	40·0267
Time of standing	1 hr.	1 hr.	1 hr.	1 hr.	1 hr.	1 hr.	1 hr.	1 hr.	1 hr.	1 hr.	1 hr.	1 hr.	1 hr.
Temperature of precipitation	15°	15°	15°	15°	15°	15°	15°	15°	15°	15°	15°	15°	15°
$KMnO_4$ required (ml.)	3·44 [1]	11·80 [1]	24·41 [1]	47·25 [1]	79·80 [1]	42·40 [1]	93·93 [1]	152·10 [2]	181·13 [2]	26·14 [3]	56·27 [3]	111·84 [3]	212·57 [3]
Na found (grs.)	0·0013951	0·0047807	0·0098895	0·0191373	0·0323192	0·0175770	0·0380395	0·0558828	0·0865465	0·0100270	0·0206976	0·0410896	0·0780992
Na present	0·0024806	0·0049612	0·0099224	0·0199810	0·0391130	0·0199810	0·0391130	0·0592543	0·0788941	0·0099224	0·0199810	0·0391130	0·0788941
Error	−0·0010855	−0·0001805	−0·0000329	−0·0008438	−0·0067938	−0·0024040	−0·0010735	−0·0033715	−0·0123476	+0·0001046	+0·0007166	+0·0019766	−0·0007949
Error per cent.	−43·75	−3·63	−0·33	−4·26	−17·36	−12·03	−2·74	−5·69	−15·65	+1·05	+3·59	+5·05	−1·05

[1] $KMnO_4$, 0·10566*N*. [2] $KMnO_4$, 0·095855*N*. [3] $KMnO_4$, 0·10008*N*.

TABLE V.

Reaction volume (ml.)	35	35	35	35	35	70	70	70	70	105	105	105	105
NaCl (grs./litre)	1·2585	2·5170	5·0341	10·1373	19·8439	10·1373	19·8439	30·0625	40·0267	5·0341	10·1373	19·8439	40·0267
Time of standing	24 hrs.	24½ hrs.	27½ hrs.	25 hrs.	24 hrs.	2½ hrs.	3½ hrs.	2½ hrs.	2½ hrs.	2½ hrs.	2½ hrs.	2½ hrs.	2½ hrs.
Temperature of precipitation	15°	15°	15°	15°	15°	15°	15°	15°	15°	15°	15°	15°	15°
$KMnO_4$ required (ml.)	3·83 [1]	12·31 [1]	25·32 [1]	48·82 [1]	86·97 [1]	45·92 [1]	94·56 [1]	151·21 [2]	182·44 [2]	26·21 [3]	55·39 [3]	107·28 [3]	210·55 [3]
Na found (grs.)	0·0015531	0·0049717	0·0102540	0·0197709	0·0352228	0·0189598	0·0382966	0·0555540	0·0670278	0·0100539	0·0203500	0·0394528	0·0773575
Na present	0·0024806	0·0049612	0·0099224	0·0199810	0·0391130	0·0199810	0·0391130	0·0592543	0·0788941	0·0099224	0·0199810	0·0391130	0·0788941
Error	−0·0009275	+0·0000105	+0·0003316	−0·0002101	−0·0038902	−0·001383	−0·0008164	−0·0037003	−0·0118663	+0·0001315	+0·0003690	+0·0003398	−0·0015366
Error per cent.	−37·33	+0·21	+3·34	−1·05	−9·94	−6·91	−2·09	−6·24	−15·04	+1·33	+1·85	+0·86	−1·95

[1] $KMnO_4$, 0·10566*N*. [2] $KMnO_4$, 0·095855*N*. [3] $KMnO_4$, 0·10008*N*.

Except for the highest concentration the error is positive and small (see Diagram 1, curve 3), the explanation being that the triple salt may be completely precipitated with slight occlusion of the precipitating reagent (due to large excess reagent).

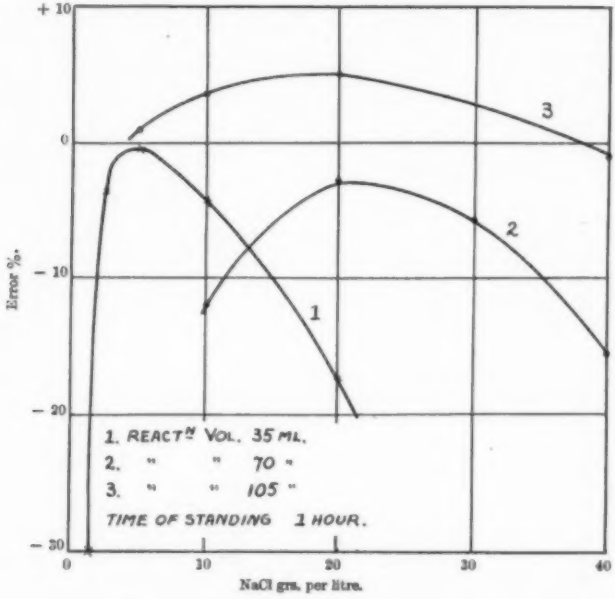

DIAGRAM 1.

INFLUENCE OF CONCENTRATION AND REACTION VOLUME.

The first and last reaction volumes completely cover the concentration range from 2·5 to 40 grs. NaCl per litre, and thus render the less satisfactory intermediate 70 ml. reaction volume unnecessary.

From 2·5 to 10 grs. NaCl per litre reaction volume is 35 ml.
„ 5 to 40 „ „ „ „ „ 105 ml.

The full experimental details are presented in Tables IV and V, the error for sodium, its sign and percentage being recorded, which is also illustrated in Diagram 1. The effect of time using the three reaction volumes is given in Table V and Diagram 2; the numbered curves correspond to those of Diagram 1. The following points should be noted: reaction volume 35 ml., the curve of percentage error is simply shifted as a whole more into the positive region; this is to be expected, as the precipitation would be more complete after such long standing. Reaction volume 70 ml., the time of standing is only 2¾ hrs., and the effect on the percentage error curve is not so marked, but a slight upward movement into the positive region again occurs. Reaction volume 105 ml., no upward movement of

the curve took place, for in the shorter time of standing precipitation was complete. Owing to such small variations of the percentage error, it was not worth while increasing the time of standing beyond 1 hr.

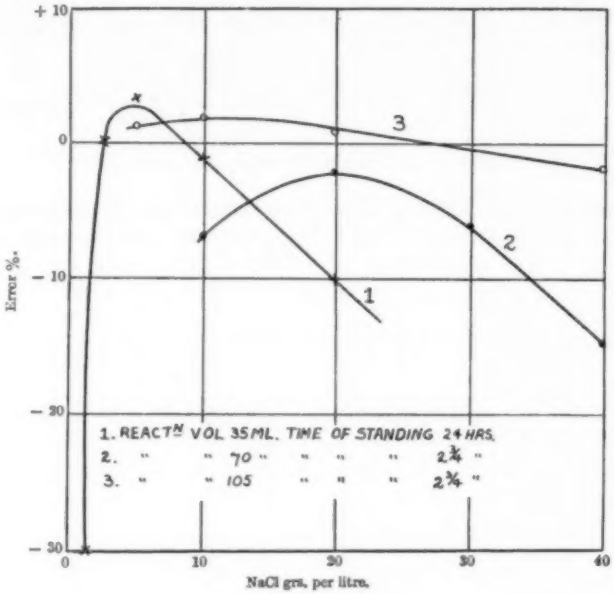

DIAGRAM 2.

INFLUENCE OF CONCENTRATION AND REACTION VOLUME.

ERRORS ARISING FROM THE PRESENCE OF METALLIC IONS.

Potassium.—The concentration of $\overset{+}{K}$ was varied from 0 to 49·8 (KCl) grs. per litre; the concentration of sodium chloride was maintained constant at 5·0341 grs. per litre and the reaction volume was constant at 35 ml. The method of analysis employed for sodium was precisely as that described in Table IV. No appreciable error results until a concentration of 37·5 grs. KCl per litre is reached. The initially slight negative error is converted into a slight positive one within this range of concentration. (Cf. Diagram 3 and Table VI.) Above this concentration of 37·5 grs. KCl per litre the positive error becomes extremely large; this is due to the precipitation of a potassium salt, probably potassium uranyl acetate, and not potassium zinc uranyl acetate, for sodium can be replaced by no other alkali metal in the triple acetate.[7] In the same table is included an experiment using a concentrated sodium chloride solution (NaCl 40 grs. per litre approx.) and a potassium chloride solution of 24·9 grs. per litre, reaction volume being 105 ml. Comparing this result with experimental data in Table IV, last column, it will be noted that the presence of potassium in this concentration and reaction volume has no appreciable effect.

TABLE VI.

Influence of $\overset{+}{K}$ on Sodium Determination.

NaCl (grs./litre) .	5·0341	5·0341	5·0341	5·0341	40·0267
KCl present .	0·0	0·1245	0·1867	0·2490	0·1245
Na found .	0·0098895	0·0100454	0·0100782	0·0129929	0·0780662
Na present .	0·0099224	0·0099224	0·0099224	0·0099224	0·0788941
Error . .	−0·0000329	+0·0001230	+0·0001558	+0·0030705	−0·0008279
Error per cent.	−0·33	+1·24	+1·57	+30·94	−1·05

Time of precipitation 1 hr. Temperature 15° C.

Ammonium.—The effect of ammonium chloride on the precipitation of the triple salt is a negative error which increases proportionally to the

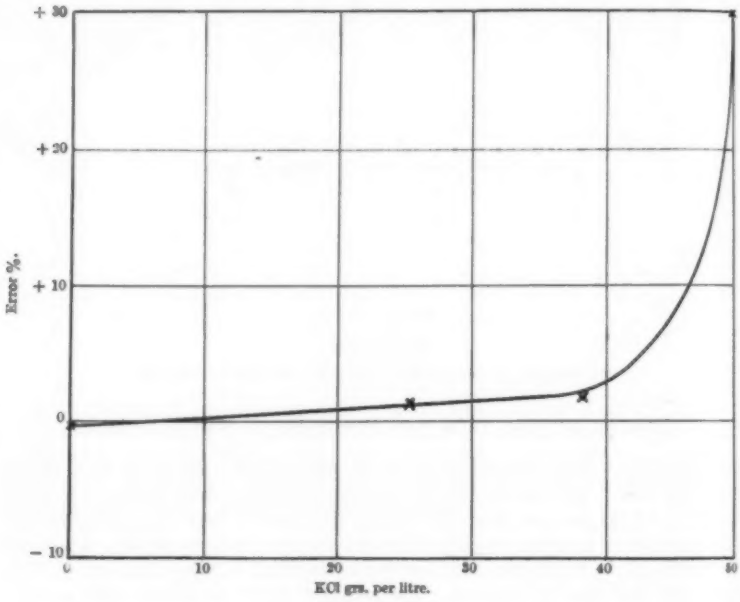

DIAGRAM 3.

INFLUENCE OF POTASSIUM ON SODIUM DETERMINATION.

ammonium chloride concentration. This is shown in Table VII and Diagram 4. The error becomes large after an ammonium chloride concentration of 25 grs. per litre is reached, and, therefore, the solution should be freed from ammonium salts by the usual process before sodium is estimated. This applies also to the estimation of sodium by dihydroxytartaric acid (cf. previous contribution). The explanation of such a large negative error is probably the formation of zinc and uranyl double salts with ammonium chloride respectively.[8]

TABLE VII.

Influence of NH_4Cl *on Sodium Determination.*

NaCl (grs./litre) .	5·0341	5·0341	5·0341	5·0341
NH_4Cl present .	0·0	0·12362	0·24723	1·23615
Na found . .	0·0098895	0·0096137	0·0095142	0·0082137
Na present . .	0·0099224	0·0099224	0·0099224	0·0099224
Error . .	−0·0000329	−0·0003087	−0·0004082	−0·0017087
Error per cent. .	−0·33	−3·11	−4·11	−17·22

Time of precipitation 1 hr. Temperature 15° C. Reaction volume 35 ml.

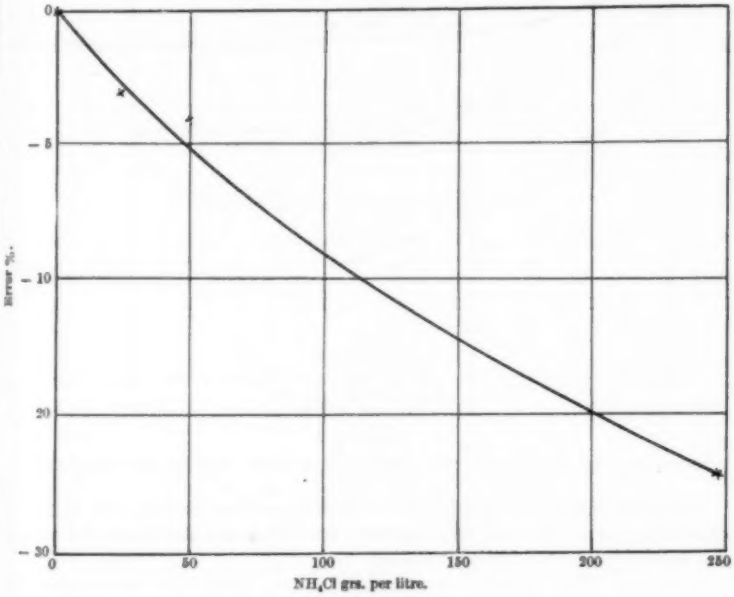

DIAGRAM 4.

INFLUENCE OF NH_4Cl ON SODIUM DETERMINATION.

Magnesium.—The presence of the magnesium ion causes a small negative error even in large concentration, and this is shown in Diagram 5, curve 1, the exact data for correction of sodium when estimated in the presence of magnesium being given in Table VIII, first three columns. Sodium can be estimated without serious error in the presence of appreciable quantities of magnesium. Ratio $MgCl_2 : Na = 26 : 1$ gives an error of 0·23 m. gr. in the reaction volume employed.

Magnesium and Ammonium.—Diagram 5 and Table VIII indicate that increasing quantities of ammonium chloride in the presence of the magnesium ion cause a large increasing negative error in the determination of sodium, viz. the curves in the diagram are displaced further into the

negative region of error, and become more inclined or concave to the axis of zero error as the ammonium chloride increases.

Sodium cannot be estimated in the presence of magnesium and ammonium salts if the magnesium concentration exceeds 5 grs. per litre of magnesium chloride and the ammonium concentration exceeds 12·5 grs. per litre of ammonium chloride. It is important to note here that the concentrations of these salts should be low for accurate work; higher concentrations are frequently encountered in analytical work, and this necessitates their removal.

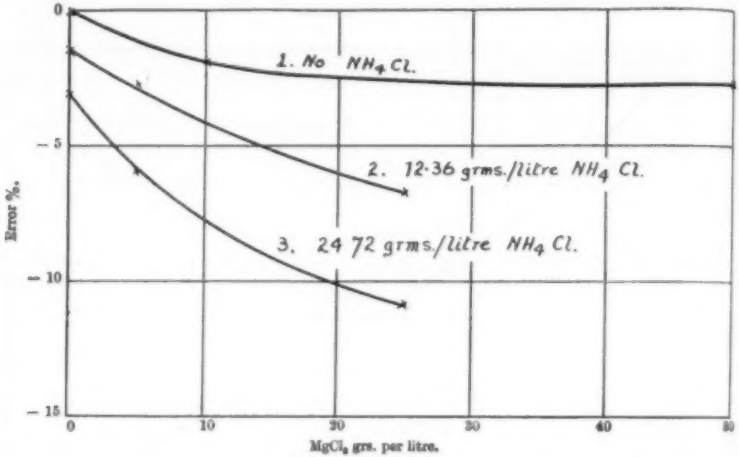

DIAGRAM 5.

INFLUENCE OF MAGNESIUM AND AMMONIUM IONS ON SODIUM DETERMINATION.

Ammonium and magnesium individually gave low results, but the error obtained when both ions were present was much greater than the sum of the errors due to the individual ions.

Calcium.—The calcium ion in similar concentration to the magnesium ion has a similar effect, causing only a small negative error even in high concentration (refer to Table IX and Diagram 6).

TABLE IX.

Influence of Ca *and* NH_4 *Ions on Sodium Determination.*

NaCl (grs./litre)	5·0341	5·0341	5·0341	5·0341	5·0341
$CaCl_2$ present	0·0	0·25350	0·0	0·02535	0·12675
NH_4Cl present	0·0	0·0	0·12362	0·12362	0·12362
Na found	0·0098895	0·0097048	0·0096137	0·0092273	0·0092445
Na present	0·0099224	0·0099224	0·0099224	0·0099224	0·0099224
Error	−0·0000329	−0·0002176	−0·0003087	−0·0006951	−0·0006779
Error per cent.	−0·33	−2·19	−3·11	−7·00	−6·83

Time of precipitation 1 hr. Temperature 15° C. Reaction volume 35 ml.

TABLE VIII.

Influence of Mg and NH_4 Ions on Sodium Determination.

NaCl (grs./litre)	5·0341	5·0341	5·0341	5·0341	5·0341	5·0341	5·0341	5·0341
$MgCl_2$ present	0·0	0·05104	0·25520	0·0	0·02552	0·12760	0·0	0·02552
NH_4Cl present	0·0	0·0	0·0	0·06181	0·06181	0·06181	0·12362	0·12362
Na found	0·0098895	0·0097372	0·0096620	0·0097081	0·0096492	0·0092598	0·0096137	0·0093366
Na present	0·0099224	0·0099224	0·0099224	0·0099224	0·0099224	0·0099224	0·0099224	0·0099224
Error	−0·0000329	−0·0001852	−0·0002604	−0·0001543	−0·0002732	−0·0006626	−0·0003087	−0·0005858
Error per cent.	−0·33	−1·86	−2·62	−1·55	−2·75	−6·68	−3·11	−5·90

Time of precipitation 1 hr. Temperature 15° C. Reaction volume 35 ml.

Calcium and Ammonium.—In the presence of ammonium chloride calcium shows a marked similarity in behaviour to magnesium in the presence of the same salt. Regarding the estimation of sodium in the presence of these two ions, remarks similar to those in the previous section under *magnesium and ammonium* apply here. The calcium should not exceed a concentration of 5 grs. calcium chloride per litre, and the ammonium chloride concentration should be low. The total error for sodium in the presence of calcium and ammonium is greater than the sum of the errors due to the individual ions. Owing to the close similarity of calcium with magnesium, it was considered unnecessary to proceed with further experimental work on the influence of calcium and ammonium on the precipitation of the sodium triple salt, this fact being shown in Diagram 5.

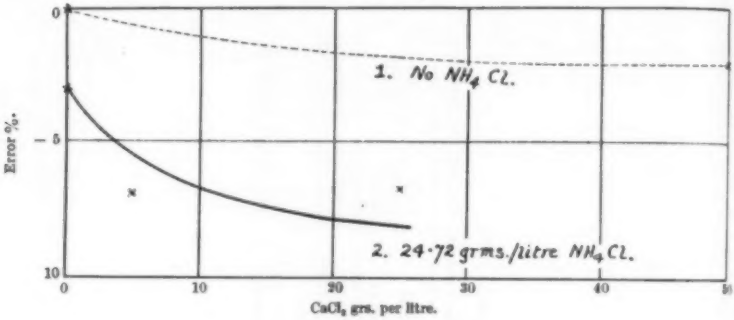

DIAGRAM 6.

INFLUENCE OF CALCIUM AND AMMONIUM IONS ON SODIUM DETERMINATION.

Investigations are now being carried out on a simple method for the estimation of potassium suited for oil-field waters, the results of which will form a subsequent paper in this series of contributions.

We express our indebtedness to Professor A. W. Nash and Dr. A. R. Bowen for their interest in these series of investigations.

Department of Oil Engineering and Refining,
University of Birmingham.

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A FURTHER NOMOGRAPHIC STUDY OF OIL PIPE-LINE DESIGN.*

By L. V. Woodhouse Clark, B.Sc. (Eng.) (Vict.), A.M.I.Mech.E. (Assoc. Member), Reza Fallah, B.Sc. (Student Member), and A. W. Nash, M.Sc., M.I.Mech.E., F.C.S., F.Inst.F. (Member).

In a previous paper † dealing with the nomographic study of pipe-line design the Authors dealt briefly with the principles underlying nomography, and explained the construction of a nomograph for determining diameter or pressure drop, given certain factors all of which are definitely obtainable. It was pointed out that the formula used was applicable only to computations falling within the turbulent region. The new formula to be discussed here is again applicable only to the same region.

In the previous paper the value of the friction factor "f" for substitution in the pipe-flow formula was of the form $f = a + bx^n$, since it is claimed that this law represents the variations of the coefficient more accurately than does the law of the form $f = bx^n$, where f = friction factor, x = Reynolds number, and a, b, and n are constants. Evidence to this effect is to be found in the results of work carried out by Professor C. H. Lees,‡ who expressed the mean curve drawn through the points obtained by plotting

$$\frac{F}{\rho v^2} = \phi\left(\frac{vd}{\nu}\right) \text{ in the form } \phi\left(\frac{vd}{\nu}\right) = a + b\left(\frac{\nu}{vd}\right)^n = a + bx^n$$

This is the form previously used, and the resultant nomograph was rather complicated on account of the addition sum occurring on the right-hand side of the equation.

The nomograph previously presented permitted the calculations of diameter or pressure drop only, and although it could have been modified to enable other calculations to be made, any further scales added would merely have increased the complications.

It was therefore decided that a further nomograph be prepared to supplement the results of the previous one, and to permit the determination of Brake Horse Power corresponding to given diameters. In addition, a simplified nomograph was essential, and with this end in view a new formula had to be devised.

The well-known pipe-flow formula $h = \dfrac{4flv^2}{2gd}$ has again been used, and the value for "f" has been so adjusted that when its value is substituted in this formula the curve obtained falls almost exactly on the curve obtained by using the experimental value of "f." At the higher and lower values of

* Paper received May 16th, 1934.

† "A Nomographic Study of Oil Pipe-line Design," L. V. W. Clark, R. Fallah, and A. W. Nash, *Proc. World Petr. Congr.*, 1933, I, 534–539.

‡ C. H. Lees, "On the Flow of Viscous Liquids through Smooth Circular Pipes," *Proc. Roy. Soc., A.*, Vol. XCI., 1914, pp. 46–53.

"f" the variation is slight, and at the intermediate points the two curves coincide exactly. This procedure has enabled a much simpler nomograph to be constructed with no great loss of accuracy.

The formulæ suggested for the value of the friction factor "f" are

$$f = 0{\cdot}08\left(\frac{\mu}{vd\rho}\right)^{0{\cdot}25},\ f = 0{\cdot}09\left(\frac{\mu}{vd\rho}\right)^{0{\cdot}25},\ \text{and}\ f = 0{\cdot}06\left(\frac{\mu}{vd\rho}\right)^{0{\cdot}2}$$

The values used in the computation of the nomograph were $\left(\frac{\mu}{vd\rho}\right)^{0{\cdot}25}$, and an average value between 0·08 and 0·09 which agreed best with the actual available pipe-line data.

The value so obtained for "f" satisfies both experimental and practical results over the range most frequently used. This value was substituted, therefore, in the pipe-flow formula and the other factors h, l, v, g, and d were converted into terms of every-day usage, so that the formula became

$$P = \phi[\mu, \rho, Q, d] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which P = pressure drop in lb./sq. inch.
μ = absolute viscosity in centipoises.
ρ = density of the fluid.
Q = quantity of oil pumped in barrels per hour.
d = diameter of pipe in inches.
l = length of pipe in miles.

In formula (1) P is the pressure drop in lb. per sq. in. which the pumps must supply, and the total pressure will be $P \times \frac{\pi d^2}{4}$. This total pressure multiplied by the velocity of the oil will be a measure of the Hydraulic Horse Power, *i.e.* H.H.P. $\propto P \times Q$, or, when all the terms are in the form required, H.H.P. $= \frac{P \cdot Q}{2451}$.

If the pump to be used has an efficiency, e, the Brake Horse Power necessary for the operation of the pump is

$$\text{B.H.P.} = \frac{\text{H.H.P.}}{e} = \frac{P \cdot Q}{2451 \cdot e}$$
$$= \phi[\rho \cdot v \cdot Q \cdot d \cdot e]$$

The construction of the nomograph follows the simple rules on nomography given in the previous paper, since the equation is of the form

$$f_3(w) = f_1(u) \times f_2(v)$$

As in the previous example, the limits of the scales can be extended to suit individual requirements, but those given will cover all the most probable conditions in the case of crude oils and medium distillates.

Given the quantity in barrels per hour to be pumped, the absolute viscosity in centipoises, the density of the fluid, the percentage efficiency of the pump, and the diameter of the line in inches, it is possible to calculate the Brake Horse Power per mile required to pump the given fluid against the frictional resistance only. The Static Head must be considered separately, and the B.H.P. necessary to pump the fluid against this head

must be added to the B.H.P. necessary to overcome the frictional resistance in order to obtain the total B.H.P. required.

The advantage of this nomograph over those usually used in the literature is twofold: (1) the operations are simplified; (2) the economic size of line can readily be chosen, as explained below.

An hypothetical example will explain the manner in which to read the nomograph, the data being chosen at random.

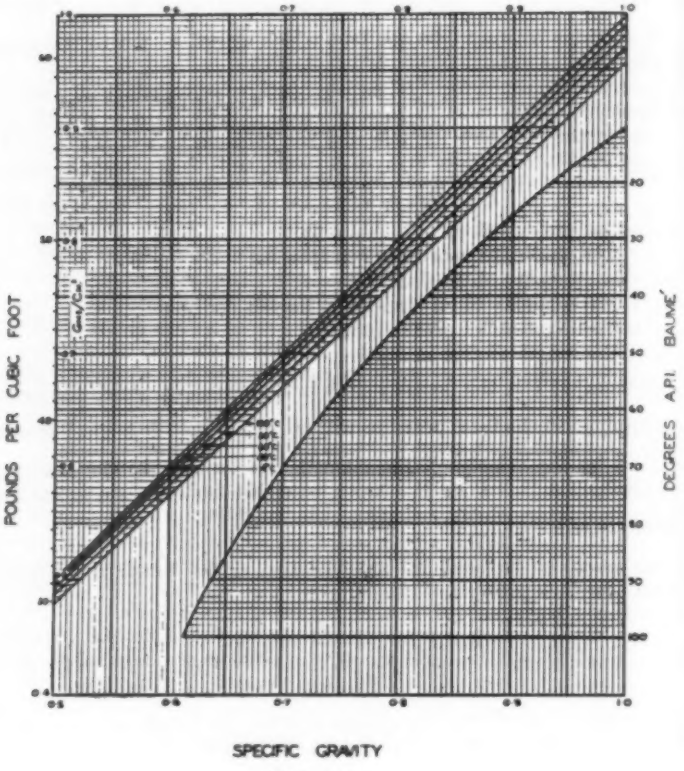
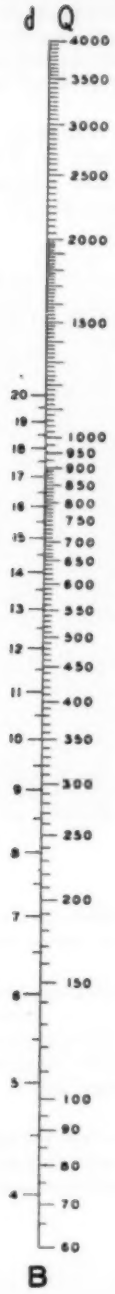


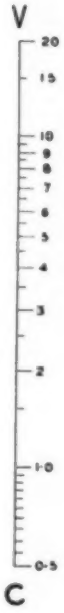
CHART 1.

Example.—To read Brake Horse Power per mile when the diameter in inches, quantity to be pumped in barrels per hour, density of the fluid, absolute viscosity in centipoises, and efficiency of the pump are available.

$d = x$ inches.
$Q = 1000$ barrels per hour.
$\rho = 1{\cdot}0$.
$\mu = 10$ centipoises.
$e = 70$ per cent.

μ – VISCOSITY IN CENTIPOISES.
ρ – DENSITY IN C.G.S. UNITS.
d – DIAMETER IN INCHES.
Q – QUANTITY IN BARRELS PER HOUR.
e – EFFICIENCY.
V – VELOCITY IN FEET PER SECOND.





KEY FOR H.P AND d

ρ	—	μ	—	D
D	—	e	—	E
E	—	Q	—	D
H.P	—	D	—	d

KEY FOR V

Q — D — V

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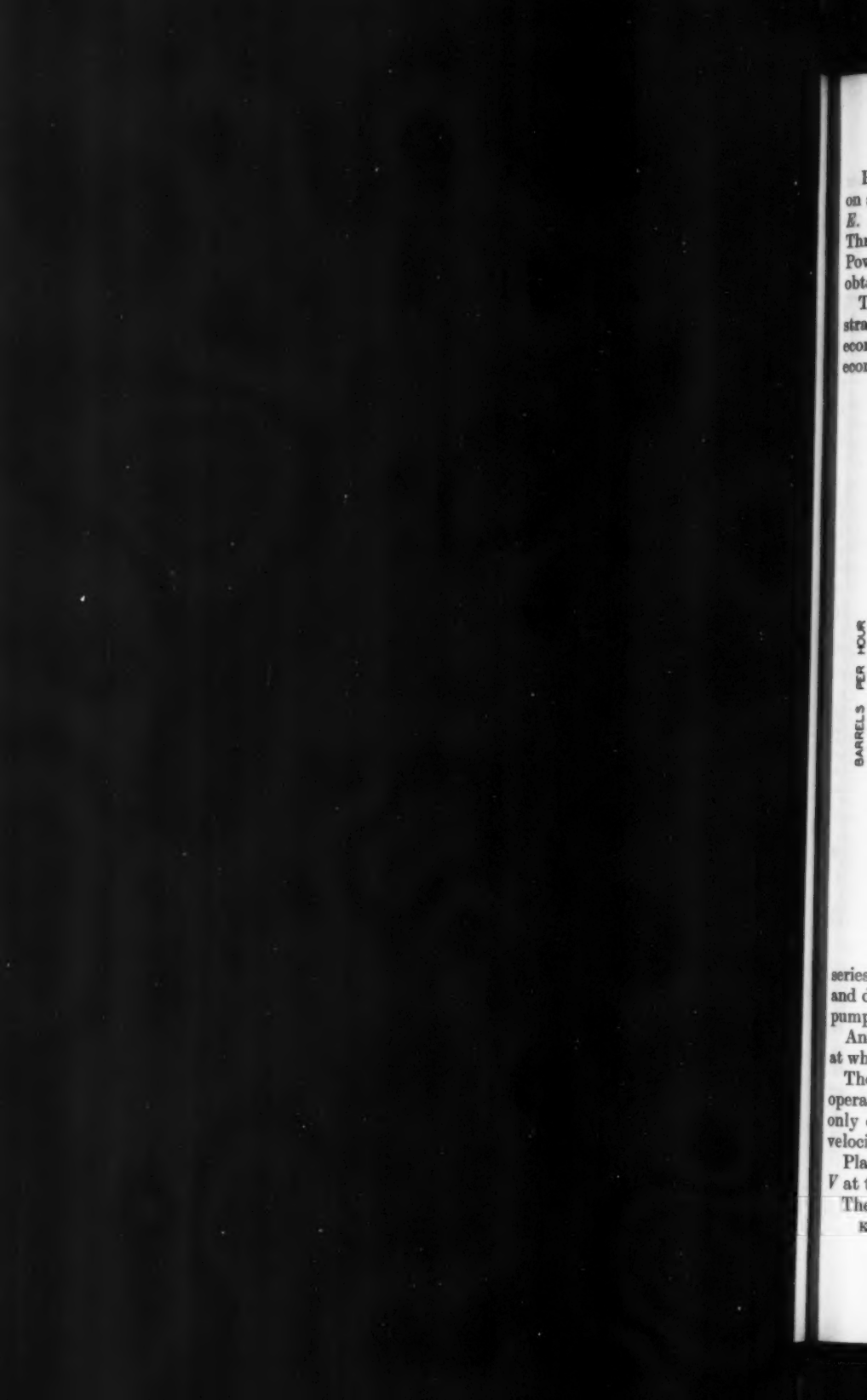


Place a straight edge to cut scale ρ at 1·0 and scale μ at 10 and mark on scale line D. Align this point and 70 on scale e and mark on scale line E. Through mark on scale line E and 1000 on scale Q mark on scale line D. Through this mark $\phi[\rho \cdot \mu \cdot Q \cdot e]$ and through x on scale d read Brake Horse Power on scale H.P. If d is equal to 10 in., the value of the H.P. thus obtained is 5·45 B.H.P. per mile.

The point on the D scale corresponding to $\phi[\rho \cdot \mu \cdot Q \cdot e]$ is always on a straight line joining the diameter to the corresponding B.H.P., so that the economic diameter of the pipe can be determined to correspond with the economic size of the pump. Thus, by swinging the index line through a

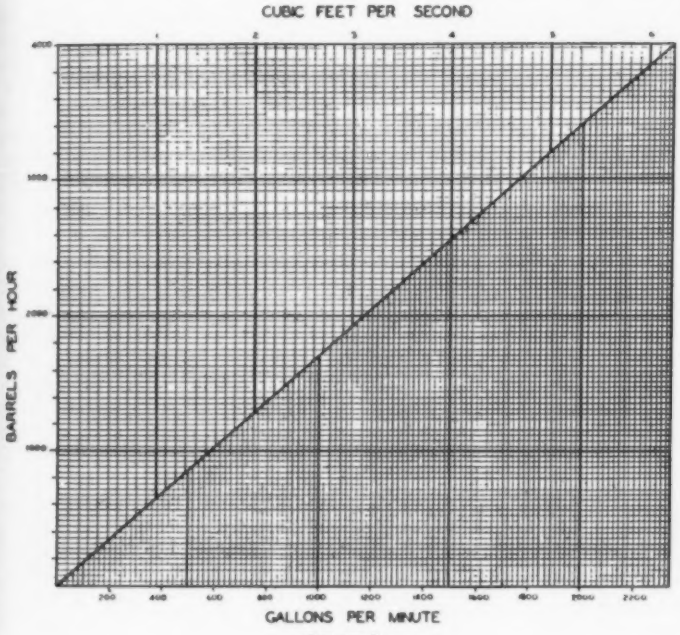


CHART 2.

series of diameters, a corresponding series of horse powers can be obtained, and depending on the cost of the pipe and the cost per horse power of the pump, the economic sizes can be chosen.

Another factor which enters into the design of oil pipe-lines is the velocity at which a given quantity of fluid will flow through a given line.

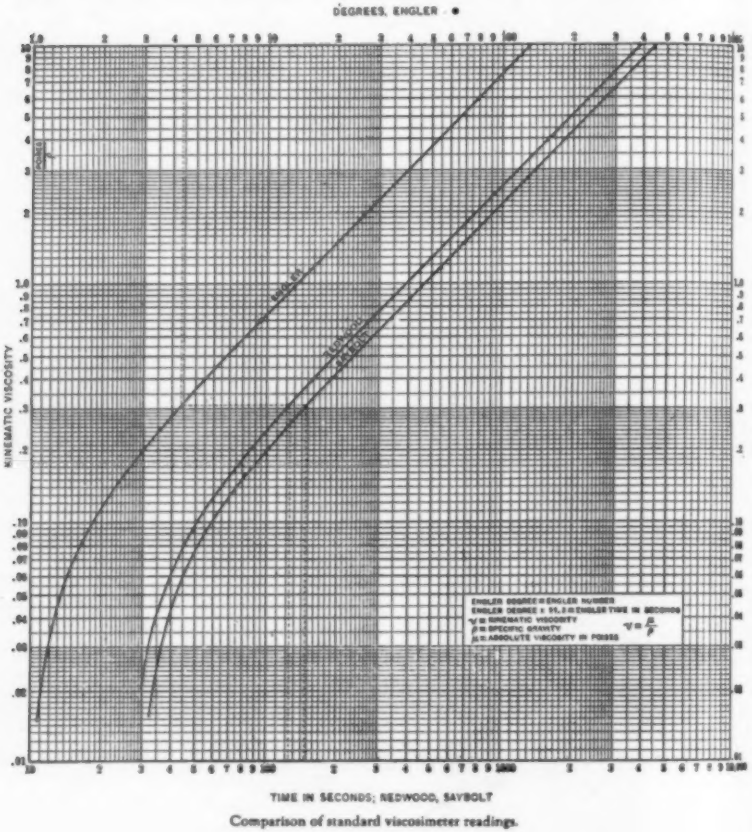
There is a limiting velocity of flow above which it is inadvisable to operate. Since velocity is a function of quantity and diameter, there is only one diameter for a given quantity which will permit of this limiting velocity.

Place a straight edge to cut scale Q at the value of the quantity and scale V at the value of the velocity. The diameter can then be read on scale D.

The units used in the formula from which the nomograph has been drawn

are not self-consistent ones, and to assist in the conversion of any other units into those required, charts 1, 2, and 3 have been prepared.

Chart 1 enables A.P.I. Baumé, pounds per cub. ft., and specific gravity to be converted into density.



Comparison of standard viscosimeter readings.

CHART 3.

Chart 2 enables cub. ft. per second and Imperial gallons per minute to be converted into barrels per hour.

Chart 3 enables the kinematic viscosity to be determined from different standard viscometer readings. The kinematic viscosity thus obtained multiplied by $\rho \times 100$ gives the absolute viscosity in centipoises.

THE DETERMINATION OF PLATE EFFICIENCY IN FRACTIONATING COLUMNS FOR COMPLEX MIXTURES.*

By A. J. V. Underwood, D.Sc., M.I.Chem.E., F.I.C.

In previous papers [1,2] on distilling columns, methods were described for calculating the number of ideal plates required for a given fractionation, and comparing this figure with the number of plates required in practice for the same separation under the same conditions of reflux ratio, etc., to obtain the "overall plate efficiency." This efficiency is a convenient measure of the performance of the column referred to an ideal column as a standard, but, being an average figure for the column as a whole, it does not indicate any variations in efficiency from one plate to another, nor any variations in efficiency for the plates between different components of the mixture. A knowledge of such variations is clearly of importance in column design.

Lewis and Wilde [3] have described a test on a petroleum fractionating column in which plate efficiency is considered only for two components at the cut point, and calculations are made using Raoult's Law with a correction factor. A method is outlined in the following for carrying out a test on a column in operation in order to ascertain the efficiency of each plate for all components of the mixture. The method is not limited to mixtures, the components of which follow Raoult's Law.

The efficiency of an individual plate—that is, the "individual plate efficiency"—is generally taken as the ratio of the change in composition of the vapour effected by the plate to the change in composition, which would result if the vapour, after passing through the plate, were in equilibrium with the liquid on it. This efficiency can be calculated for each component of the mixture if there are given the composition of the vapour below the plate, the composition of the vapour above the plate, the composition of the liquid on the plate, and the composition of the vapour that would be in equilibrium with that liquid. To obtain these data for a given column would involve an analysis of the liquid on every plate and of the vapour rising from every plate. It will be shown that it is only necessary to determine liquid compositions, as the vapour compositions can be calculated from these by the use of material and thermal balances only. By this means the difficulty of obtaining true samples of vapour and the labour of analysing them are avoided. Briefly stated, the procedure is to determine by analysis the composition of the liquid on each plate of the column. For any section between two plates, the composition of the vapour is calculated from the composition of the reflux at that section, which is the composition of the liquid on the upper plate. The composition of the vapour rising from each plate is thus found. The composition of the vapour which would be in equilibrium with the liquid on that plate is obtained from equilibrium data

* Paper read at a joint meeting with the Institution of Chemical Engineers on March 21st, 1934.

for the mixture, or may be determined experimentally for the liquid compositions in question. The efficiency of each plate for each component of the mixture is then readily calculated. Where certain components are present in only small amounts—for example, high-boiling components in the upper part of a column or low-boiling components in the lower part of a column—the efficiency figures obtained for such plates for these components will be more seriously affected by experimental error than the corresponding figures for plates where these components occur in appreciable amounts. When dealing with mixtures such as petroleum fractions, where individual components are not identifiable, suitable intervals on the true boiling-point curve are taken as representing individual components.

The method of calculation varies slightly according to the three main types of distillation encountered in practice. The first case is that of a mixture where the components are miscible in all proportions. The second is where two immiscible liquids are present in the column, the vapours of both being saturated : this is the case of distillation with saturated steam. It occurs in the distillation of petroleum fractions with the aid of steam when the temperature and pressure conditions in the column are such that water is present on the plates. The third case is distillation with superheated steam when the temperature and pressure conditions are such that water is present only in the column in the form of superheated vapour.

The following symbols are used :

a, b, c.—The mol fractions of the different components in the liquid at any point.
A, B, C.—The mol fractions of the different components in the vapour at any point.
P, F, W.—The mols of product, feed, and residue per unit time respectively.
V, O.—The mols of vapour and reflux per unit time respectively.
h.—The total heat of 1 mol of liquid.
H.—The total heat of 1 mol of vapour.
Q.—The heat absorbed in the reflux condenser per unit time.

The position of a plate, counting from the top of a column, is denoted by the suffix n. The suffixes p, f, w refer to the distillate, feed, and residue respectively. Indices such as a, b, etc., denote reference to those particular components. Thus h_n^a is the total heat of 1 mol of component a in the liquid form at the temperature of the nth plate.

Case I. All Components Completely Miscible.—For a concentrating column, by taking balances for total material, each component and heat above a section between the nth and $(n+1)$th plates, the following equations are obtained :

$$V_{n+1} = O_n + P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$V_{n+1}A_{n+1} = O_n a_n + Pa_p;\ V_{n+1}B_{n+1} = O_n b_n + Pb_p; \text{ etc.} \quad . \quad (2)$$

$$V_{n+1}H_{n+1} = O_n h_n + Q + PH_p \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since the total heat of a mixture is equal to the sum of the total heats of its components, assuming no heat of mixing,

$$H_{n+1} = A_{n+1}H_{n+1}^a + B_{n+1}H_{n+1}^b + \quad . \quad . \quad . \quad . \quad (4)$$

and

$$h_n = a_n h_n^a + b_n h_n^b + \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

so that equation (3) becomes

$$V_{n+1}(A_{n+1}H^a_{n+1} + B_{n+1}H^b_{n+1} + \ldots) = O_n(a_n h^a_n + b_n h^b_n + \ldots) + Q + PH_p.$$

Substituting the values of $V_{n+1}A_{n+1}$, $V_{n+1}B_{n+1}$, etc., given by equations (2), this becomes :

$$O_n\{a_n(H^a{}_{+1} - h^a_n) + b_n(H^b_{n+1} - h^b_n) + \ldots\} = Q + P(H_p - H^a_{n+1}a_p - H^b_{n+1}.b_p \ldots) \quad . \quad (6)$$

From this equation O_n, the reflux from the nth plate, can be calculated, given the composition of the reflux and product and the thermal data for the components of the mixture. From the value of O_n, the value of V_{n+1} is obtained from equation (1) and the values of A_{n+1}, B_{n+1}, etc., from equation (2). The composition of the vapour rising from each plate is thus calculated, using only material and thermal balances.

In certain cases equation (6) takes a simpler form. If the temperature difference between the nth and $(n+1)$th plates is small, H^a_{n+1} is approximately equal to H^a_n and $H_{n+1} - h^a_n = L^a_n$, the molal latent heat of component a at the temperature of the nth plate.

Equation (6) then becomes :

$$O_n(a_n L^a_n + b_n L^b_n +) = Q + P(H_p - H^a_{n+1}a_p - H^b_{n+1}b_p) \quad . \quad (7)$$

Also $H_p = H^a_p.a_p + H^b_p.b_p + \ldots$

and if the temperature difference throughout the column is not large, H^a_p is approximately equal to H^a_{n+1}, and equation (7) becomes :

$$O_n(a_n L^a_n + b_n L^b_n + \ldots) = Q \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It will be seen that equations (6), (7), and (8) hold good for weight units as well as molal units.

Taking equation (8) in molal units, if Trouton's Rule applies, then $L^a_n = L^b_n = \ldots = L$ approximately, so that $O_n L(a_n + b_n + \ldots) = Q$, or $O_n L = Q$ since $a_n + b_n + \ldots = 1$. This is the ordinary equation for constant molal reflux.

For an exhausting column, if balances are taken for the upper part of the column, equations similar to (1), (2), and (3) are obtained, modified by the inclusion of appropriate terms relating to the feed. Alternatively the balances may be taken for the lower part of the column, so that the equations are obtained in a form involving the heat input to the kettle and the amount and composition of the residue.

Case II. Distillation with Saturated Steam.—It is assumed that water is immiscible with the other components of the mixture. The symbols previously used for liquid and vapour compositions and quantities are taken to apply to the non-aqueous portion of the mixture at any point.

The following additional symbols are used :

S.—The mols of steam per unit time in the vapour at any point.

s.—The mols of water per unit time in the liquid at any point.

p.—The mols of steam per unit time leaving the reflux condenser with the product.

π_n.—The total pressure above the nth plate of the column.

θ_n.—The pressure of saturated water vapour at the temperature of the nth plate.

Assume that a petroleum product is being distilled, so that the non-aqueous portion of the mixture at any point can be designated for convenience as hydrocarbons. Then material balances for total hydrocarbons and individual components gives, as before:

$$V_{n+1} = O_n + P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$V_{n+1}A_{n+1} = O_n a_n + Pa_p;\ V_{n+1}B_{n+1} = O_n b_n + Pb_p;\ \text{etc.} \quad . \quad (2)$$

From a steam balance $$S_{n+1} = s_n + p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and for a thermal balance

$$V_{n+1}H_{n+1} + S_{n+1}H^s_{n+1} = O_n h_n + s_n h^s_n + Q + PH_p + pH^s_p \quad . \quad (10)$$

where H^s and h^s denote the total heat of 1 mol of steam and water respectively.

Making the same substitutions as were used in deriving equation (6), we obtain

$$O_n\{a_n(H^a_{n+1} - h^a_n) + \ldots\} + S_{n+1}H^s_{n+1} = Q + s_n h^s_n + P(H_p - H^a_{n+1}a_p \ldots) + pH_p \quad . \quad (11)$$

Unlike equation (6), equation (11) does not give directly the value of O_n, as it contains the unknown terms S_{n+1} and s_n. Although S_{n+1} and s_n are connected by equation (9), s_n is still unknown. It is practically impossible to obtain an experimental value of s_n by analysis of the liquid on any plate, owing to the difficulty of ensuring that a representative sample is taken containing the correct proportions of the two immiscible liquids.

An additional equation is, therefore, required in order to solve equation (11). This is obtained from the relation between the partial pressures of water vapour and hydrocarbon vapour, namely:

$$\frac{\theta_{n+1}}{\pi_{n+1} - \theta_{n+1}} = \frac{S_{n+1}}{V_{n+1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

This involves the assumption that the partial pressure of the water in the vapour is equal to the vapour pressure of water at the temperature of the plate or, in other words, that the water in the liquid is in equilibrium with its vapour at that temperature. Although this is not necessarily true, it probably represents a very close approximation.

From equation (12):

$$S_{n+1} = \frac{\theta_{n+1}}{\pi_{n+1} - \theta_{n+1}} \cdot V_{n+1} = \frac{\theta_{n+1}}{\pi_{n+1} - \theta_{n+1}}(O_n + P) \quad . \quad (13)$$

Also from equations (9) and (13).

$$S_{n+1}H^s_{n+1} - s_n h^s_n = S_{n+1}(H^s_{n+1} - h^s_n) + ph^s_n.$$

Substituting this value in equation (11) gives:

$$O_n\{a_n(H^a_{n+1} - h^a_n) + \ldots\} + \frac{\theta_{n+1}}{\pi_{n+1} - \theta_{n+1}}(O_n + P)(H^s_{n+1} - h^s_n) = Q + P(H_p - H^a_{n+1}a_p \ldots) + pH^s_p - ph^s_n \quad . \quad (14)$$

From this equation O_n can be found, since a_n, a_p, etc., are known from the analyses of the hydrocarbon portions of the reflux and product. The values of V_{n+1}, A_{n+1}, S_{n+1}, and s_n can then be found from equations (1), (2), (9), and (12).

Where water in the condensate from the reflux condenser is separated, and is not returned to the column, the amount thus separated must be added to the term p in equation (9), and its heat content must be added to the term pH'_p in equation (10). It will be seen that this will make only a very small difference in equation (14).

In working out a practical example, many of the terms in equation (14) will be negligibly small. It will be seen that, as was shown for equation (6), when the temperature does not vary greatly through the column :

$$O_n\{a_nL^a + b_nL^b + \ldots\} + \frac{\theta_{n+1}}{\pi_{n+1} - \theta_{n+1}}(O_n + P)L' = Q + pL'$$

or
$$O_n\left\{a_nL^a + b_nL^b + \ldots + \frac{\theta_{n+1}L'}{\pi_{n+1} - \theta_{n+1}}\right\} = Q + pL' - \frac{\theta_{n+1}PL'}{\pi_{n+1} - \theta_{n+1}} \quad . \quad (15)$$

If π^1 and θ^1 are the total pressure and the partial pressure of steam in the reflux condenser, then $\frac{p}{P} = \frac{\theta^1}{\pi^1 - \theta^1}$ and, if the temperature variation through the column is small, the last two terms in equation (15) will be nearly equal, so that, as an approximation :

$$O_n\left\{a_nL^a + b_nL^b + \ldots + \frac{\theta_{n+1}L'}{\pi_{n+1} - \theta_{n+1}}\right\} = Q.$$

Also, if the molal latent heats of the hydrocarbon components are equal, so that $L^a = L^b = \ldots$

then
$$O_n\left\{L^a + \frac{\theta_{n+1}L'}{\pi_{n+1} - \theta_{n+1}}\right\} = Q.$$

It should be noted that even if the temperature variation in the column is fairly small, the factor $\frac{\theta_{n+1}}{\pi_{n+1} - \theta_{n+1}}$ may have a much larger variation, particularly if θ_{n+1} is relatively large.

If Trouton's Rule can be applied, so that $L^a = L' = L$ approximately, and if variations in temperature through the column are neglected entirely, so that constant molal reflux is assumed, then :

$$O_nL\left(1 + \frac{\theta}{\pi - \theta}\right) = Q,$$

or
$$O_n = \frac{Q(\pi - \theta)}{\pi L}.$$

For an exhausting column the method is modified in the same way as was described for Case I.

Case III. Distillation with Superheated Steam.—If the temperature in

the column is such that the steam is superheated, water in liquid form cannot be present on the plates, so that s_n, which appears in equations (9) and (10), must be zero. From the former equation is found the value of S_{n+1}, the amount of steam passing any plate in unit time, which is constant through the column. In equation (11), therefore, since $s_n = 0$ and S_{n+1} is known, it remains only to find H^s_{n+1} in order to be able to calculate O_n. The total heat of the superheated steam, H^s_{n+1}, depends not only on its temperature, which is known, but also on its partial pressure, which, being the difference between the total pressure and the vapour pressure of the hydrocarbon portion of the vapour, is not known. However, the heat content of superheated steam, of a given temperature, varies little with the partial pressure. As an extreme example, the total heat of steam at 400° F. and 1 lb./sq. in. partial pressure is 1240 B.Th.U/lb., while at 400° F. and 250 lb./sq. in. pressure, which is its saturation pressure, the total heat is 1207 B.Th.U/lb. Consequently a very rough estimation of the partial pressure involves a negligible error in the value of H^s_{n+1} and in its use in equation (11). Obviously the partial pressure of the steam can also be assumed constant throughout the column without appreciable error.

O_n is thus found from equation (11), and the quantity of vapour and its composition are found from equations (1) and (2) as before.

If sidestreams are taken off the column at any points, they must be allowed for in the material and thermal balances. As the amount, composition and heat content of each sidestream are known, the methods described above can be applied when suitable modification is made.

Radiation losses are allowed for by adding to the term Q in equations (6) and (10) the amount of heat lost by radiation from that part of the column above the $(n + 1)$th plate.

Method of Procedure in Test.—From the foregoing it will be seen that the procedure of the test can be summarised as follows:

(1) Determine the amounts, compositions, and heat contents of the feed, distillate, residue, and any sidestreams.
(2) Determine the pressures at the top and bottom of the column and find the pressure on each plate on the assumption of a linear variation through the column.
(3) Determine the heat absorbed in the reflux condenser and the heat supplied to the column in the kettle or at other points.
(4) From the data in (1) and (3) a heat balance can be obtained for the whole column, and the radiation loss found either from this balance or by calculation.
(5) Determine the temperature on each plate and the composition of the liquid on each plate by analysis. In the case of petroleum products this would be a true boiling-point analysis. In columns of large diameter, the composition of the liquid may vary from point to point on a plate, and samples should be drawn off at points which will indicate representative compositions.
(6) By the methods which have been described, calculate the composition of the vapour rising from each plate.
(7) Determine, from equilibrium data, the composition of the vapour which would be in equilibrium with the liquid on each plate.

In the case of petroleum products the equilibrium data could be obtained by using Raoult's Law with suitable correction factors determined experimentally for the particular products under consideration.

(8) From (6) and (7) the efficiency of each plate for each component of the mixture can be calculated.

Reliable data on plate efficiency under different conditions are a prime necessity for future progress in design. It is usually assumed that an efficiency of the order of 60–75 per cent. may be expected in practice, but the experimental data in support of this assumption are unfortunately scanty. If plate efficiency is low, then modification of plate design offers scope for substantial progress. If, however, plate efficiency is already fairly high, there is little room for improvement along these lines, as the theoretical limit imposes a maximum. In these circumstances substantial improvements in fractionating equipment could only be made in other directions, possibly involving a radical departure in design from the present type of column.

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THE MINERAL CONTENT OF PETROLEUM.*

By E. Longobardi.

The inorganic constituents of crude petroleum are dealt with, special reference being made to the presence of vanadium, which the Author claims to have been first discovered in Argentine petroleum by himself and N. Camus in 1911.

The Author mentions that the discovery was not a result of systematic investigations relating to the mineral components of petroleum, but came about through an attempt to establish a relationship between a lignite from San Rafael and a crude petroleum from the same locality.

This lignite had been previously studied by J. J. J. Kyle, who had found it to contain vanadium to the extent of 38·22 per cent. of the ash, which totalled 0·63 per cent. of the lignite.

The petroleum gave 0·0377 per cent. of ash, of which 11·93 per cent. was V_2O_5, corresponding to 0·0045 per cent. calculated on the petroleum. The vanadium content of the lignite was thus 53 times that of the petroleum.

Up till the year 1913, the known inorganic constituents of petroleum comprised the elements Si, As, P, Al, Fe, Ca, Mg, Cu, Ag, Au, V, and Na.

Through the work of various investigators, whose published results are briefly reviewed, this list has been increased by the addition of Ti, Pb, Sn, Ni, Mn, Cr, Ba, Sr, K, and Li.

It is pointed out that almost all the elements mentioned occupy the four first decades of Clarke's classification as modified by Vernadky, according to which the components of the terrestrial crust are grouped in accordance with the proportions in which they enter into its composition.

Only three of them (Pb, Ag, and Au) belong to the fifth, seventh, and eighth decades.

Vanadium occupies fourth place in the group forming the fourth decade, and, according to Vernadky, the great mass of its atoms are found in a state of dispersion, it being apparently proved that it concentrates in organic matter, and to this may be due its association with asphaltic matter.

Various theories to account for the presence of the above-mentioned elements in petroleum are cited and discussed. Iron, for instance, may come from pipe-lines and tanks or from ferruginous rocks; silicates may be found in solution in small quantities due to the tendency of such substances to form soaps.

In general, the composition of the petroleum ash may indicate the class of rock which has been in contact with the oil. For example, the presence of lime and magnesia in oils from Ohio suggests a solvent action on the dolomitic rocks of that region.

Again, the mineral content has been used as indicative of the origin of the oil itself, as exemplified by a Beaumont crude, referred to by Thiele as containing phosphorus, and therefore being confirmatory of Engler's theory of the animal origin of oil.

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The Author quotes extensively from papers presented before the Institution of Petroleum Technologists and from the discussions resulting therefrom. The work of Guthrie on heavy-grade Egyptian crude is referred to, as well as Sutherland's reference to an asphalt found in the Andes. Hackford's theories regarding the origin of Mexican crude, Dunstan's analysis of Persian petroleum ash, and Ramsay's paper on the significance of nickel are discussed at some length, as well as Dewhurst's contribution to one of the discussions.

Reference is also made to the presence of vanadium in various lignites, bituminous shales, and natural asphalts, it being apparently established that the element is associated with these substances in too great a proportion to allow the fact to be explained only by its wide diffusion in nature.

Its presence in such bodies suggests that it can also be found in petroleum to an extent not compatible with mere coincidence, and if this could be proved, vanadium will be known as being associated with peculiar types of substances, and as forming a link between them.

Such a connection will need an explanation which will demonstrate its genetic significance.

Considerable space is devoted to the work of Fester and his pupils at the Litoral University on the geochemistry of vanadium.

Fester carried out investigations with the object of discovering the origin of vanadium in Rafaelite, and concluded that the vanadium content of this material was more or less proportional to the bituminous content, and independent of other organic matter.

The fact is mentioned that the Bergin Company in Germany had purified Mexican petroleum by absorption methods, finding that not only was sulphur absorbed, but also all the vanadium.

Fester thought that this indicated the presence in petroleum of vanadium sulphide in a state of colloidal solution.

The Author and Camus had found the ratio $\frac{V_2O_5}{S}$ in Rafaelite to be 9·27, whilst in crude petroleum from San Rafael the ratio was 9·65. They were thus in accord with Fester in supposing that the vanadium in Rafaelite was derived from the crude petroleum and from its mother substance, and that filtration through the earth would have the effect of eliminating vanadium by absorption, but would not incorporate it in the bitumen.

Fester is also quoted with reference to his tentative hypothesis in which he suggests a genealogical sequence in which vanadium coming from eruptive rocks passes to the state of pentoxide dissolved in water; thence, by means of precipitation, together with iron and nickel, to the state of V_2S_3 by reaction with hydrogen sulphide produced by thiobacilli, and finally the formation of mud with the intervention of other microflora and animal remains and the production of bituminous shales, petroleum, asphalt, and asphaltites.

The Author points out that if Fester's supposition is correct, then it follows that the precipitation of vanadium and nickel in the form of sulphide would take place in shallow surroundings.

Reference is made to the work of W. B. Shirey on the metallic constituents of crude petroleum, which incorporates the largest number of analyses with an exact determination of the components of petroleum. Shirey is quoted

as stating that there is a certain quantitative relation between the content of nickel and vanadium, and whilst nickel is apparently present in ash from all crude oils in regular quantity, vanadium appears to be associated more particularly with asphaltic crudes, and may be found in the merest traces, or not at all, in some petroleums with a paraffin base.

With regard to other metallic constituents, no regularity of any kind has been discovered.

The paper concludes with a brief reference to the commercial importance of petroleum as a source of vanadium and other elements, mention being made of the fact that flue dust from the combustion of Mexican fuel oil in oil-tank ships had been collected and sent to British steelworks, the vanadium recovered being sufficient to pay for the cost incurred.

It is also suggested that petroleum from San Rafael might also be utilised as a source of vanadium, since it contains 45 grs. of V_2O_5 per ton.

J. McC. S.